



**AUTOMONOUS EXPERIMENTATION OF CARBON NANOTUBE  
GROWTH USING RESPONSE SURFACE METHODS**

THESIS

William Adorno III, Captain, USAF

AFIT-ENS-MS-15-M-113

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William Adorno III, BS

Captain, USAF

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**Abstract**

Advances in hardware and software technology have led to the development of automated research systems. The Air Force Research Laboratory (AFRL) utilizes the Adaptive Rapid Experimentation and Spectroscopy (ARES) system to synthesize carbon nanotubes. The AFRL researchers are investigating different approaches that can improve the experimental capability of ARES from automation to autonomy. Carbon nanotubes are discussed as an emerging technology for many applications, but AFRL has yet to discover what factors optimize the nanotube initial growth rate. In this study, experimental planning software was written for ARES that autonomously designs and executes experiments based on the Response Surface Methodology (RSM). RSM is a statistically-based method of sequentially planning experiments to find the optimal settings of independent variables that optimize the value of a dependent response variable. This thesis discusses the development and early success of the initial version of the planning software. As this is a relatively new research area spurred by recent advancements in materials research technology, detailed discussion is also provided on the unique challenges of creating autonomous research robots.

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# AUTOMONOUS EXPERIMENTATION OF CARBON NANOTUBE GROWTH USING RESPONSE SURFACE METHODS

## **I. Introduction**

### **1.1 Autonomous Systems**

The Air Force (AF) Chief Scientist's 2010-2030 science and technology vision, "Technology Horizons", states "a key finding is the need, opportunity, and potential to dramatically advance technologies that can allow the Air Force to gain capability increases, manpower efficiencies, and cost reductions through far greater use of autonomous systems in essentially all aspects of Air Force" (Chief Scientist, 2010:130). In response to this vision, the Air Force Research Laboratory (AFRL) released a strategy to develop and improve autonomous systems. The terms automation and autonomy are often used synonymously, but AFRL developed clear definitions that separate these two levels of system operability. An automated system can function with little or no human involvement, but is limited to performing specific actions from the initial system design (AFRL, 2013). An autonomous system includes "a set of intelligence-based capabilities that allow it respond to situations that were not pre-programmed or anticipated in the design" (AFRL, 2013). Automation is only a fraction of autonomy, so increasing the level of autonomy in automated systems should improve manpower efficiency and reduce costs as described by the AF Chief Scientist.

In 2012, the Defense Science Board (DSB) also released a report, "The Role of Autonomy in Department of Defense Systems", which discusses many different applications and benefits of autonomy (DSB, 2013). However, the DSB report fails to

mention the use of autonomy in experimental systems. Automated experimental systems can perform multiple experiments based on the inputs of the researcher. After a set of experiments, the researcher must analyze the results and then determine another set of experiments to progress towards a certain objective. The addition of autonomy to an experimental system can eliminate the need for frequent intervention by the researcher.

Experimental autonomy leaves more time for the researcher to focus on subject-matter research rather than the design and execution of experiments. Scientific researchers may not have a strong familiarity with Design of Experiments (DOE), so autonomous software can reduce costs by planning fewer experiments to achieve the same or better results.

Any autonomous system can fail if the user's trust in the software is lost. Trust is established through successful results, as well as, an effective interface that communicates progress and results to the user. A quality understanding of the methodology and techniques applied by the software helps to foster trust.

Additionally, the user's patience is a major factor in autonomous experimental systems. If the user does not trust the autonomous experimental system, the process may not be allowed to reach its end state. With a loss of patience, the user might decide to terminate the experimental process before the software is able to reach a significant conclusion.

To promote trust and ensure that the user remains patient with the software, several objectives can be accomplished. The following objectives are desired for autonomous DOE software to operate effectively over a long period of time:

1. The user interface is understandable and easy to use.
2. Decisions made by the program are virtually equivalent to what a human expert in DOE would decide in the same situation.
3. Display the status of each step of the experimental process to provide awareness of important decisions made by the software.
4. Optimize the desired response variable within the experimental process, so the user is not regularly required to select additional inputs.
5. Plan experiments within the feasible region of execution to ensure system operates properly.

Accomplishment of these five objectives will facilitate the usefulness and longevity of the autonomous DOE software.

## **1.2 Carbon Nanotube Growth Research**

In the 17<sup>th</sup> century, Muslim weapon forgers designed legendary weapons known as Damascus Sabers. During the Crusades, these sabers were highly effective against European warriors, because they were supremely sharp, strong, and flexible. In 2006, scientists discovered that the secret behind the Damascus Saber's superiority was that the weapon forgers had unintentionally created carbon nanotubes within the steel (Fountain, 2006). Scientists today can intentionally develop carbon nanotubes, but there are still many challenges in production to overcome. The tensile strength and flexibility of carbon nanotubes can lead to many potential applications and an important role in the future of nanotechnology. Some of potential applications include a space elevator,

fighting cancer cells, replacing Kevlar, and solar cells. Before any of that is possible, scientists must identify what factors significantly affect carbon nanotube growth.

AFRL is one of many parties interested in carbon nanotube experimentation. The Soft Matter Materials Branch (RXAS) at AFRL acquired a machine, the Adaptive Rapid Experimentation and Spectroscopy (ARES) system, that can eventually execute up to one hundred carbon nanotube experiments in a single day (Nikolaev et al., 2015). ARES applies laser-induced Chemical Vapor Deposition (CVD) to synthesize carbon nanotubes. CVD synthesizes carbon nanotubes with three main components: a heat source, a hydrocarbon gas mixture, and a catalyst. The researchers can adjust the settings of these components and several other factors to produce carbon nanotubes with different growth characteristics and properties. They would like to characterize nanotube production as a function of these factors. However, the researchers are not deeply familiar with DOE and the planning of rigorous experiments to reach their research goals. The AFRL/RXAS researchers desire an experiment planner computer program that autonomously characterizes and optimizes the initial growth rate of carbon nanotubes.

The ARES system includes several other experiment planner options that apply machine learning techniques. The RSM planner software is the first that includes an actual DOE-based approach to optimize a response variable. Machine learning techniques are reliant on the database of previous experimental results. The current databases were not obtained using DOE principles. RSM is capable of exploring the entire region of operability to find potential solutions. Machine learning techniques are computationally rigorous and typically difficult for novice users to understand, while

RSM requires little computation and is fairly simple to understand. The researchers expect the RSM planner to operate conveniently and to obtain significant findings faster than the other options, because of its ability to optimize and apply efficient experimental designs.

### **1.3 Response Surface Method**

Response Surface Methodology (RSM) is a procedure of statistical techniques that is useful when modeling a problem that includes many factors influencing the response of interest (Montgomery, 2008:478). RSM is well-suited to work with carbon nanotube experimentation due to the large number of factors and because the researchers believe the response surface is highly nonlinear (Nikolaev et al., 2015). RSM can be applied to this problem, because all of the variables are continuous and response optimization is desired. A computer program is designed and coded for ARES to autonomously plan experiments by following the RSM approach. This program is coded in the C# language for compatibility with the ARES software. The program is capable of experimenting with up to six different factors with the goal of maximizing the initial growth rate of carbon nanotubes.

Before the RSM process starts, the researchers can adjust several input categories to include the initial search location, factor level sizes, and factor level boundaries. The program plans the appropriate experiments based on the initial inputs and the current stage of the RSM process. The process continues until the initial growth rate stops increasing in value. A local and possibly global solution is found when the response surface appears in the canonical form of a local maximum. Once this solution is

obtained, the program ceases to plan experiments and reports the optimal setting of each factor and the maximum response value. Maximizing the initial growth rate is the first step towards maximizing carbon nanotube production. The results of the RSM process should provide insight into what factors significantly affect the initial growth rate.

#### **1.4 Limitations and Scope**

The program is designed to operate with no more than six factors and maximizes one response variable. These factors are the only variables of current interest to the researchers. Of the six factors, half are continuous process variables and the other half are mixture variables. Future deviations to the number and type of variables will require a major adjustment to the program's source code. The researchers are also interested in maximizing another continuous response variable, the catalyst lifetime. The current settings in ARES did not allow enough time during each experiment to capture results of this variable. Due to the large of percentage of catalyst lifetime results that cannot be obtained, this RSM process only focuses on the initial growth rate response. Several other categorical responses are important to the researcher, such as whether a synthesized carbon nanotube is single or multiple walled. RSM is only appropriate for continuous response variables, so categorical or binary responses are not included in this study.

#### **1.5 Research Objectives**

The following objectives are defined for this thesis.

1. Determine the most suitable experimental designs to model six factors with a specialization to include three mixture variables.



2. Incorporate the experimental designs into an RSM process to maximize the initial growth rate in a quick and efficient manner.
3. Create a user interface that fosters trust and awareness with the researcher.
4. Automate the decision process concerning which set of experiments are selected for each stage of the RSM process.
5. Determine the challenges of autonomous experimentation.

## **1.6 Thesis Overview**

The remainder of this document is organized as follows. This first chapter introduces the topic of interest and the research objectives. The second chapter provides an in-depth review on important background information and the analytical techniques applied in this thesis. The third chapter contains a detailed description of the methodology used to accomplish the research objectives. The fourth chapter includes and describes the results from the implementation of the RSM experiment planner. Finally, the fifth chapter will discuss analytical conclusions and recommendations for future research.

## **II. Background**

This chapter is a comprehensive overview of the subject matter and the analytical techniques that are applied in this study. The first section is an overview of Response Surface Methodology (RSM). The second section explains carbon nanotube growth factors and response variables. The third section discusses important considerations for the Adaptive Rapid Experimentation and Spectroscopy (ARES) system. The fourth section discusses the advantages and disadvantages of the current ARES experimental planners. The fifth section explains the analytical techniques applied within the RSM process.

### **2.1 Response Surface Methodology Overview**

A statistical approach to experimental design helps to draw meaningful conclusions from data (Montgomery, 2008:11). It is difficult to understand the true relationships between the inputs and outputs of a system without a structured experimental design. In the 1920s and 1930s, Sir Ronald A. Fisher's statistical analysis of agricultural data led to the three primary principles of DOE: randomization, blocking, and replication (Montgomery, 2008:21). His later work led to factorial designs and Analysis of Variance (ANOVA) which are also cornerstones of DOE. Applications of statistical design continued to increase during the industrial era with the advent of RSM by Box and Wilson in 1951 (Montgomery, 2008:21). RSM expands on DOE to solve problems that require mapping a response surface, response optimization, and selection of optimal operation conditions (Myers et al., 2009:8). RSM is limited to problems that contain continuous independent and response variables.

RSM can be a useful technology in the formulation of new products due to its capability to optimize response variables and find desired operating conditions. Most RSM applications are sequential procedures that can involve multiple iterations of experimental designs and analysis (Myers et al., 2009:6). This experimental procedure is performed within the feasible operability region encompassed by the independent variable space (Myers et al., 2009:7). In problems involving more than three independent variables, mapping the response surface over the entire region of operability is usually impractical and cumbersome. Therefore, the sequential procedure consists of smaller regions of experimentation and statistical models that are utilized to search the operability region for the optimal response location (Myers et al., 2009:8). When near the optimal response location, a higher-order statistical model is applied to the region of experimentation to better characterize the response surface and discover important results.

## **2.2 Carbon Nanotube Growth Factors and Response**

### ***2.2.1 Growth Factors***

The Adaptive Rapid Experimentation and Spectroscopy (ARES) system performs Chemical Vapor Deposition (CVD) to synthesize carbon nanotubes (Rao et al., 2012). CVD requires three main ingredients: a heat source, a hydrocarbon gas mixture, and a metallic catalyst (Nikolaev et al., 2015). ARES provides heat using a high-powered laser. The hydrocarbon gas mixture is a combination of up to three different gases: ethylene, hydrogen, and argon. The catalyst is chemical compound typically consists of at least one of the following elements: cobalt, iron, nickel, or aluminum (Nikolaev et al., 2015). The ARES system can also control total pressure and water

concentration. The total pressure is the pressure of the gas chamber and is completely independent from the hydrocarbon gas mixture. The water concentration acts as a cooling agent for the catalyst to prolong the catalyst lifetime (Nikolaev et al., 2015).

The catalyst type certainly influences carbon nanotube growth, but it is not a factor that is changeable between individual experiments. The catalyst type is held constant for each replication of the RSM process. For laser power, the independent variable is the calibrated temperature in Celsius at initial growth. The calibrated temperature does slightly differ from the planned temperature on a regular basis. The total pressure is adjusted and measured in units of torr. Water concentration is adjusted and measured in parts per million (ppm). Temperature, pressure, and water concentration are process variables, and are adjusted independently without impacting the setting of another variable (Cornell, 2011:354). The hydrocarbon gas mixture contains three different mixture variables. Mixture variables differ from process variables, because the proportion of one of the components must decrease if another proportion is increased (Smith, 2007:3). Since mixture variables are not independent factors, different techniques are used to include them with process variables in the same experimental design and linear model. The mixture variables are adjusted in ARES as flow rates (standard cubic centimeters per minute), but are measured in the planner as percentages of the total mixture.

Engineering (actual) units are used when the planner is providing the experiment settings to ARES. However, all of the design creation and analysis is executed in coded units. Coded units enable orthogonal test matrices when properly designed and evenly scale each factor to make coefficient estimates comparable (Montgomery, 2008:290).

All factor levels are coded to fall within the  $[-1, 1]$  range; minimum settings to -1, maximum settings to 1. The coded units included in the first-order design are -1, 0, and 1 for the low, center, and high factor levels, respectively.

### ***2.2.2 Response Variable***

The overall goal of the current carbon nanotube research is to maximize production. Total production is function of the rate of production, production sustainability, and time. Carbon nanotube production acts in a similar manner. ARES monitors a G-band which is indicative of graphitic carbon (Rao et al., 2012). Basically, this monitor measures carbon nanotube growth over time. When plotted over time, two other important parameters are: the initial growth rate and the time constant. These two parameters are shown in the growth curve example in Figure 2.1 as  $\nu$  and  $\tau$ , respectively.

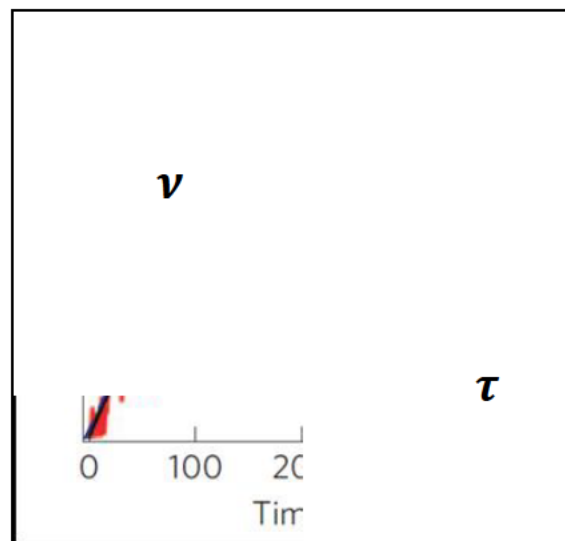


Figure 2.1. Carbon Nanotube Growth Curve Example.  
(Reprinted from (Rao et al., 2012) with permission from the Nature Publishing Group)

The initial growth rate  $\nu$  represents the estimated initial slope of the predicted G-band line. The time constant  $\tau$  is also referred to as the catalyst lifetime, because it represents when the growth curve levels off. The growth curve is estimated by the self-exhausting exponential formula (Rao et al., 2012)

$$G(t) = \nu\tau[1 - \exp(-t/\tau)] \quad (1)$$

where  $t$  is *time* in seconds. ARES automates the creation of this growth curve and the parameter estimation, but occasionally the researcher must manually estimate the parameters when there is an issue with data capture.

When the maximum G-band is reached at the expiration of catalyst lifetime, Equation 1 reduces to  $\nu\tau$ . The researchers are particularly interested in maximizing  $\nu\tau$  in order to maximize production. However, the time constant is difficult to obtain during each experiment, as the result can extend beyond the allotted time for data capture. Due to the high frequency of experiments that do not include valid results, the time constant response variable is not included in the RSM process. Fortunately, maximizing the initial growth rate still provides a positive contribution towards maximizing  $\nu\tau$ .

### 2.3 ARES System Overview

The ARES system is the overarching software that controls and monitors the carbon nanotube experimentation process (Nikolaev et al., 2015). Experimental planners are an additional feature of ARES but are only instructions to perform certain sets of experiments or runs. These experiment plans are written to a data file that acts as the main line of communication between ARES and the planner. The planner is not involved with the physical experimentation process after the experiment plan is submitted.

Actually, the planner program is completely closed after the submitting the planner data file. RSM is a continuous process, so an input/output data system must keep track of the planner's status and necessary data after each set of planned experiments.

This study focuses on autonomy in experimental planning, but there are many aspects of ARES that are not yet autonomous. The researcher must perform a series of various calibrations and alignments on the system before each set of experiments. The amount of experimentation per each set is also limited. Experiments are performed one patch at time and each patch contains 25 silicon pillars (Rao et al., 2012). Theoretically, up to 25 experiments can execute in a single experiment plan, but this is rarely a feasible option. The researcher uses a camera and microscope to identify which pillars are available on each patch. Typically, many pillars are unavailable due to previous experimentation or are scattered with debris from neighboring pillars that overheat during experimentation (Nikolaev et al., 2015). To accommodate for the restriction in the number of experiments, the planner should continually provide experiment sets less than about 15 runs. Sets of only a few experiments are also not preferred due to the amount of setup time required.

The amount of experimentation is limited on each patch, so it very likely that results originate from multiple patches. Analysis of previous growth data revealed a possible change in the initial growth rate depending on the patch used to experiment (Nikolaev et al., 2015). The blocking principle is a useful technique to minimize the potential increase in variance from the change in patch (Montgomery, 2008:13). Blocking is explained in further detail in Section 2.5.2 for the first-order design and Section 2.5.5 for the second-order design. The only other major nuisance factors the

researchers identified were laser temperature related. The ambient temperature in the ARES lab and the laser temperature calibration seem to affect growth results (Nikolaev et al., 2015). Occasionally, the calibrator does not produce actual temperatures that are close to the planned temperatures. Unfortunately, incorporating the actual calibrated laser temperatures into the planner's analysis is not currently an option.

## **2.4 Current ARES Experiment Planners**

The RSM planner is incorporated into the list of available experimental planners on ARES. The two most prominent planners apply machine learning techniques: an artificial neural network and a random forest. Below are some of the disadvantages of these current planners:

1. The linear dependency of mixture variables is not taken into consideration.  
Without the proper mixture experimental design, other techniques tend to ignore some significant blending effects due to the linear combinations within the data.
2. Total pressure is not assessed as an independent factor and is often combined with the mixture variables to create partial pressures.
3. The planned flow rates of the mixture variables are not maximized, so it takes longer to prepare each experiment.
4. The methods are based on previous database results. Data in the current database was not obtained using experimental design principles. Methods based on predicting previous results often struggle extrapolating these results to new areas of application. Also, the database resets whenever the type of catalyst is changed.



5. The underlying analytical techniques are highly advanced, but are computationally rigorous and difficult for the ARES users to understand.
6. Instead of maximizing a response, these planners request a response target value from the user. The users do not fully understand how to adjust the target value and the degree of extrapolation that is possible.

The current planners do offer several advantages that the RSM planner is not expected to incorporate in this study:

1. There is no requirement on the amount of experiments planned in each set. Traditional experimental designs and blocking principles are limited in the minimum amount of experiments allowable in a single block.
2. The current planners do not require the success of every experiment. The successful experiments are added to the database and the unsuccessful experiments do not affect future planning.
3. Although the experiments were not designed deliberately, the current planners do incorporate previous data and any insights that may exist from data in the current database.

## **2.5 Review of RSM Techniques**

### ***2.4.1 Conversion of Mixture Variables to Ratio Variables***

Traditional RSM techniques are designed for independent variables. The inclusion of mixture variables into the process presents the decision to either adjust RSM techniques to accommodate mixture variables or convert the mixture variables to independent variables. There are many different techniques to include both mixture and

process variables in the same experimental design and regression model. A well-known technique is the Cartesian join which involves appending a mixture design onto each process variable experiment run (Smith, 2005:303). This approach has two major downfalls; many experiments are required for even the most modest design and the search path is limited to only process variables. Also, analysis of a mixture response surface is especially difficult within an automated program.

The other approach is to transform  $q$  mixture variables into  $q - 1$  independent variables. The ratio variable method, presented by John Cornell in “Experiments with Mixtures”, is particular easy to apply in an automated program (Cornell, 2011:305). The only requirement is that each ratio has a component that is included in the other ratios in the same set (Cornell, 2011:306). In this study, the three mixture variables are converted into two ratio variables to ensure that traditional RSM techniques and experimental designs are viable throughout the entire process. All coded experimental designs now include a total of five independent variables. Since ethylene is in every experiment, the percentage of this gas  $x_2$  is the denominator of both ratios to eliminate the possibility of ever dividing by zero. The percentage of argon and hydrogen gases are represented as  $x_1$  and  $x_3$ , respectively. The first ratio  $r_1 = \frac{x_1}{x_2}$  is argon per ethylene and the second ratio  $r_2 = \frac{x_3}{x_2}$  is hydrogen per ethylene. When engineering units are required, the following three equations convert the ratio variables back into mixture percentages:

$$\text{Argon (Ar): } x_1 = \frac{r_1}{1+r_1+r_2} \quad (2)$$

$$\text{Ethylene (C}_2\text{H}_4\text{): } x_2 = \frac{1}{1+r_1+r_2} \quad (3)$$

$$\text{Hydrogen (H}_2\text{): } x_3 = \frac{r_2}{1+r_1+r_2} \quad (4)$$

These three equations are derived from the two ratio formulas and the mixture requirement that  $x_1 + x_2 + x_3 = 1$ .

ARES only accepts the mixture variables in the flow rate form, so an additional conversion is required to plan experiments. The researchers want the total flow rate large to accelerate the gas insertion process. The optimal setting of flow rates is calculated with a Linear Program (LP). An LP model is a set of mathematical functions where linearity exists in both the objective and constraint functions (Hillier and Lieberman, 2005:12). The LP model has three decision variables for flow rate,  $f_1, f_2, f_3$ , that represent argon, ethylene, and hydrogen, respectively. The constraints shown in Equations 6 through 8 each include one slack variable,  $s_1, s_2, s_3$ . The LP objective function is shown in Equation 5. The constraints of the LP model are shown in Equations 6 through 11.

$$\text{Maximize:} \quad \text{Total flow} = f_1 + f_2 + f_3 \quad (5)$$

$$\text{Subject to:} \quad f_1 + s_1 \leq 20 \quad (6)$$

$$f_2 + s_2 \leq 17.2 \quad (7)$$

$$f_3 + s_3 \leq 50.5 \quad (8)$$

$$f_1 - r_1 f_2 = 0 \quad (9)$$

$$f_3 - r_2 f_2 = 0 \quad (10)$$

$$f_1, f_2, f_3, s_1, s_2, s_3 \geq 0 \quad (11)$$

Equations 6 through 8 are the constraints for the maximum flow rate setting for argon, ethylene, and hydrogen, respectively. Equations 9 and 10 are the constraints that ensure the two ratio variable relationships are achieved. Equation 11 constrains all decision variables to be non-negative.

A simplified technique was discovered to easily solve this LP within the C# environment. The LP model contains six decision variables and five constraints. Therefore, when  $r_1 > 0$  and  $r_2 > 0$ , only one variable is nonbasic or set equal to zero in the final solution (Hillier and Lieberman, 2005:110). All of the flow rates are non-zero, so one of the slack variables must be nonbasic. The nonbasic slack variable is derived through a minimum ratio analysis from the simplification of the simplex method. When argon is non-zero, the smallest value out of  $\frac{20}{r_1}$ , 17.2, or  $\frac{50.5}{r_2}$  determines if  $s_1$ ,  $s_2$ , or  $s_3$  is the nonbasic variable, respectively. When  $r_1 = 0$  or  $r_2 = 0$ , the unaffected values are assessed in the minimum ratio analysis. After the nonbasic variable is determined, the flow rate of the variable included in that constraint is set to the right-hand-side value. The other two flow rates are easily calculated using the two ratio constraint equations.

### ***2.4.2 First Order Design***

Factorial designs are particularly useful to investigate main effects and interactions on a response variable. The  $2^k$  factorial design is important for two major aspects of the RSM process: to generate the factor estimates required in the path of steepest ascent and as a building block to create other response surface designs (Myers et al., 2009:73). These designs are labeled  $2^k$  because  $k$  factors are considered at only

two factor levels. A full  $2^k$  design requires  $2^k$  experiments, but this amount can be reduced depending on what information is needed. Fractional factorial designs are based on the sparsity of effects principle that a system is largely impacted by main effects and low-order interactions rather than high-order interactions (Montgomery, 2008:321). Due to the unlikelihood of higher-order interactions, a fractional factorial design combines main effects and low-order interactions with higher-order interactions (Montgomery, 2008:322). These combined effects are referred to as aliases.

Various fractional factorial design options are compared using the design resolution method. A resolution V design ensures that no main effect or two-factor interaction is aliased with another main effect or two-factor interaction (Montgomery, 2008:324). A resolution V design produces quality main effect estimates for the path of steepest ascent and can augment easily to a second-order design (Myers et al., 2009:298). This design is also orthogonal for a model containing main effects and two-factor interactions which ensures linear independence and minimizes variance (Myers et al., 2009:286). Orthogonality is a very useful property, because it eliminates multicollinearity in the regressor variables (Montgomery et al., 2012:118). Multicollinearity is a common problem in data that is not collected from an experimental design. Multicollinearity can cause inflated or erroneous effect estimates due to the near-linear dependencies within the data (Montgomery et al., 2012:285).

For a design with five factors, a half fraction  $2^{5-1}$  produces a resolution V design. Therefore, 16 less runs are required to generate effect estimates of a similar quality. In addition to the 16 fractional factorial runs, the first-order design should include center point runs to test for lack of fit and estimate pure error. Typically, at least

three center point runs are recommended for the lack of fit test and to augment to a second-order model (Montgomery, 2008:288). Four center point runs are included in the first-order design to allow for an even distribution if blocking is necessary. The experiment order of each first-order design is randomized. Randomization is a design technique applied to minimize the effects of uncontrollable nuisance factors (Montgomery 2008:139). The full  $2^{5-1}$  design is usually difficult to accommodate, so it is split into two separate blocks of ten. Blocking is a critical noise reduction technique that ensures that any nuisance variability is not wrongfully distributed to certain effect estimates or to inflate the estimate of experimental error (Montgomery, 2008:313). The block designs are generated using the two-factor interaction for total pressure and water concentration. Through discussion with the researchers, this two-factor interaction was deemed as the most improbable to significantly affect the response (Nikolaev et al., 2015). Each block contains two center point runs and is randomized independently from the other block.

#### ***2.4.3 Lack of Fit Test***

A factorial design and the path of steepest ascent work well even in situations where the linearity assumption barely holds (Myers et al., 2009:109). However, a first-order model and design is typically inappropriate when quadratic effects are significant. Pure quadratic error is identified by testing whether the center point responses fall on the same linear plane as the factorial response results (Myers et al., 2009:110). A pure quadratic error F-test is performed on the results of each first-order design to determine the adequacy of a first-order design. The sum of squares for pure quadratic curvature is calculated with the formula (Myers et al., 2009:111)

$$SS_{Pure\ quadratic} = \frac{n_F n_C (\bar{y}_F - \bar{y}_C)^2}{n_F + n_C} \quad (12)$$

where

$n_F$  = number of factorial runs

$n_C$  = number of center runs

$\bar{y}_F$  = average of factorial response values

$\bar{y}_C$  = average of center point values

The F-statistic is the ratio of the sum of squares for pure quadratic error with the mean square for pure error. The mean square for pure error formula is calculated by the formula (Myers et al., 2009:112)

$$MS_{Pure\ error} = \frac{\sum_{center\ runs} (y_i - \bar{y}_C)^2}{n_C - 1} \quad (13)$$

where  $y_i$  is the *response value* for each center experiment. Following the first-order design experimentation, the F-statistic is compared with an F-critical value associated some confidence level,  $\alpha$ , such as 0.05 or 95 percent. Alternatively and used here, the probability that the F-statistic comes from the hypothesized central F distribution is calculated and returned as the test p-value. This comparison determines if a second-order model or the linear search process is the next course of action. This p-value represents the level of significant required to reject the null hypothesis that the current first-design is linear (Montgomery 2009:40). The p-value is generated by evaluating the F-statistic with numerator degrees of freedom of one and  $n_C - 1$  for the denominator.

#### ***2.4.4 First-order model and Path of Steepest of Ascent***

The path of steepest ascent is a first-order gradient-based optimization technique derived from the main effects of the first-order model (Myers et al., 2009:189). The first-order regression model is obtained by the formula

$$\ln \hat{v} = \beta_0 + \beta_1 r_1 + \beta_2 r_2 + \beta_3 z_1 + \beta_4 z_2 + \beta_5 z_3 + \varepsilon \quad (14)$$

where

$\hat{v}$  = predicted initial growth rate

$\beta_i$  = main effect of factor  $i$

$r_1, r_2$  = ratio variables

$z_1, z_2, z_3$  = process variables

$\varepsilon$  = random error component

Montgomery et al. (2012) list five major assumptions of regression analysis:

1. The response and regressors relationship is at least approximately linear.
2. The error term  $\varepsilon$  has a zero mean.
3. The error term  $\varepsilon$  has a constant variance  $\sigma^2$ .
4. The errors are uncorrelated (lacks autocorrelation).
5. The errors are normally distributed.

Linear regression analysis of prior initial growth rate data revealed an issue with constant variance of the model residuals. The residuals of model appeared to have a funnel-like shape when plotted against the predicted response values as shown in Figure 2.2.



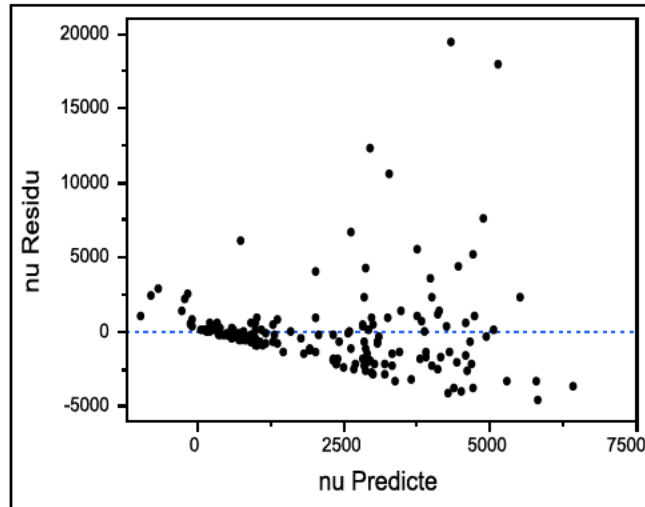


Figure 2.2. Prior Data: Residual by Predicted Response Plot

A natural log transformation is applied to the response to stabilize the variance. Figure 2.3 shows the updated residual by predicted response plot with a variance that appears constant.

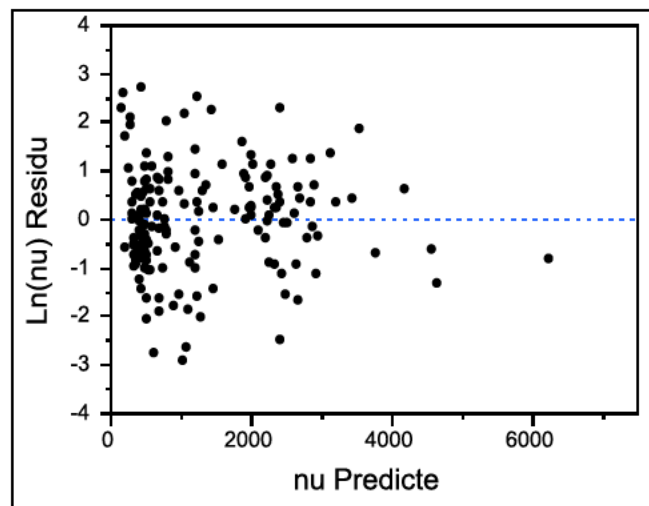


Figure 2.3. Prior Data with Transformation: Residual by Predicted Response Plot

The path of steepest ascent is generated with the unit gradient approach using the formula

$$\Delta x_j = \frac{\beta_j}{\sqrt{\sum_{j=1}^5 \beta_j^2}}, \forall j \quad (15)$$

where

$\Delta x_j$  = search gradient of factor  $j$

$\beta_i$  = main effect of factor  $j$

Each  $\Delta x_j$  is multiplied by the associated factor level size to create the increments that each factor changes during each search step. This path of steepest ascent does not include interaction terms, because even moderately large interaction effects cause a slight deviation to the true path (Myers et al., 2009:190). Steepest ascent paths using nonlinear models require solving a series of constrained nonlinear optimizations. Additional search iterations can correct large deviations to the search path.

#### ***2.4.5 Second-Order Design Augmentation and Model***

The Central Composite Design (CCD) is a popular second-order design that is created by augmenting the current first-order design with axial runs (Myers et al., 2009:298). The first-order design is resolution V which supports the estimation of main effects and two-factor interaction effects in the CCD. A CCD with five factors requires ten axial point runs to estimate quadratic effects. Axial points are spaced at a certain distance from the design center along each axis for a single factor each run (Myers et al., 2009:297). This axial distance is important in determining the variance properties of the CCD and for orthogonal blocking. Rotatability is an important property of a CCD,

because it provides a reasonably stable distribution of the scaled prediction variance throughout the design region (Myers et al., 2009: 305). Rotatability is achieved when the axial distance is  $\alpha = \sqrt[4]{F}$  with  $F$  as the number of factorial runs (Myers et al., 2009:307).

Blocking is another important consideration when the CCD is created by augmentation. Orthogonal blocking the axial point augmentation with the previous first-order design minimizes the impact of nuisance factors on the quadratic effects (Myers et al., 2009:325). To achieve orthogonal blocking, the axial distance is calculated with the formula

$$\alpha = \sqrt{\frac{F(2k + a_0)}{2(F + F_0)}} \quad (16)$$

where

$F$  = number of first-order factorial points

$F_0$  = number of first-order center runs

$k$  = number of factors

$a_0$  = number of center runs in axial block

When zero center point runs are included in the axial block, the axial distance achieves both rotatability and orthogonal blocking. Therefore, the axial distance is set to  $\alpha = 2.0$ .

The second-order model includes main effects, quadratic terms, and two-factor interaction terms. This model is calculated by the formula

$$\begin{aligned}
\ln \hat{v} = & \beta_0 + \beta_1 r_1 + \beta_2 r_2 + \beta_3 z_1 + \beta_4 z_2 + \beta_5 z_3 \\
& + \beta_{11} r_1^2 + \beta_{22} r_2^2 + \beta_{33} z_1^2 + \beta_{44} z_2^2 + \beta_{55} z_3^2 \\
& + \beta_{12} r_1 r_2 + \beta_{13} r_1 z_1 + \beta_{14} r_1 z_2 + \beta_{15} r_1 z_3 + \beta_{23} r_2 z_1 \\
& + \beta_{24} r_2 z_2 + \beta_{25} r_2 z_3 + \beta_{34} z_1 z_2 + \beta_{35} z_1 z_3 + \beta_{45} z_2 z_3 + \epsilon
\end{aligned} \tag{17}$$

where

$\hat{v}$  = predicted initial growth rate

$\beta_i$  = main effect of factor  $i$

$\beta_{ii}$  = quadratic effect of factor  $i$

$\beta_{ij}$  = interaction effect of factor  $i$  with factor  $j$

$r_1, r_2$  = ratio variables

$z_1, z_2, z_3$  = process variables

$\epsilon$  = random error component

#### 2.4.6 Canonical Analysis

The canonical analysis uses the coefficients of the second-order model to determine the location of stationary point within the design region. The stationary point can represent a minimum, maximum, saddle point, or ridge system depending on these coefficients. First, to calculate the stationary point, the  $\hat{B}$  matrix is assembled with second-order and interaction coefficients:

$$\hat{B} = \begin{bmatrix} \beta_{11} & \beta_{12}/2 & \dots & \beta_{15}/2 \\ & \beta_{22} & \dots & \beta_{25}/2 \\ & & \ddots & \vdots \\ sym. & & & \beta_{55} \end{bmatrix} \tag{18}$$

A vector of main effects  $b' = [\beta_1, \beta_2, \beta_3, \beta_4, \beta_5]$  and  $\hat{B}$  are used to calculate the stationary point  $x_s$  (Myers et al., 2009:223). The stationary point is calculated with the formula

$$x_s = -\frac{1}{2}\hat{B}^{-1}b \quad (19)$$

This stationary point is in coded units referenced from the center of the second-order design. The conversion to engineering units is applied before reporting the results to the user. The predicted response at the stationary point is calculated by the formula (Myers et al., 2009:224)

$$\hat{y}_s = b_0 + \frac{1}{2}x_s'b \quad (20)$$

### **III. Methodology**

This chapter explains the computer program that autonomously plans experiments to optimize carbon nanotube growth. The first section overviews the Response Surface Methodology (RSM) process. The succeeding sections discuss the algorithms within the sub-processes of system. The second section explains the start of the RSM process and first-order design generation flow. The third section explains the lack of fit test, the linear regression model, and the search process flow. The fourth section explains the second-order design generation, the second-order regression model, and the canonical analysis flow. The fifth section explains the analysis of solutions from the model. The last section discusses the challenges of applying RSM procedures to create experimental autonomy within the Adaptive Rapid Experimentation and Spectroscopy (ARES) system.

#### **3.1 RSM Model Overview**

The RSM process begins with manual input of the experimental boundary, the factor level sizes, and the initial start location. The planner creates a randomized first-order design with the information from the user's inputs. Center point experiments are included in the first-order design to test for lack of fit. The lack of fit test determines the significance of quadratic curvature in the current response surface. If the surface appears linear, the planner calculates a first-order regression model to find the gradient used to search outside of the region. The search progresses until the response variable stops increasing in value. The planner executes a series of first-order designs and linear searches until the surface appears non-linear. When the lack of fit test detects a significant curvature in the response surface, additional axial runs are augmented to the

first-order design to complete a second-order design. The planner calculates a second-order regression model from the augmented design and performs canonical analysis. The planner displays the optimal response value and the corresponding factor level settings to the user. Users can save the solution and compare with previous results to improve future RSM processes. Figure 3.1 shows the flowchart of the RSM overview.

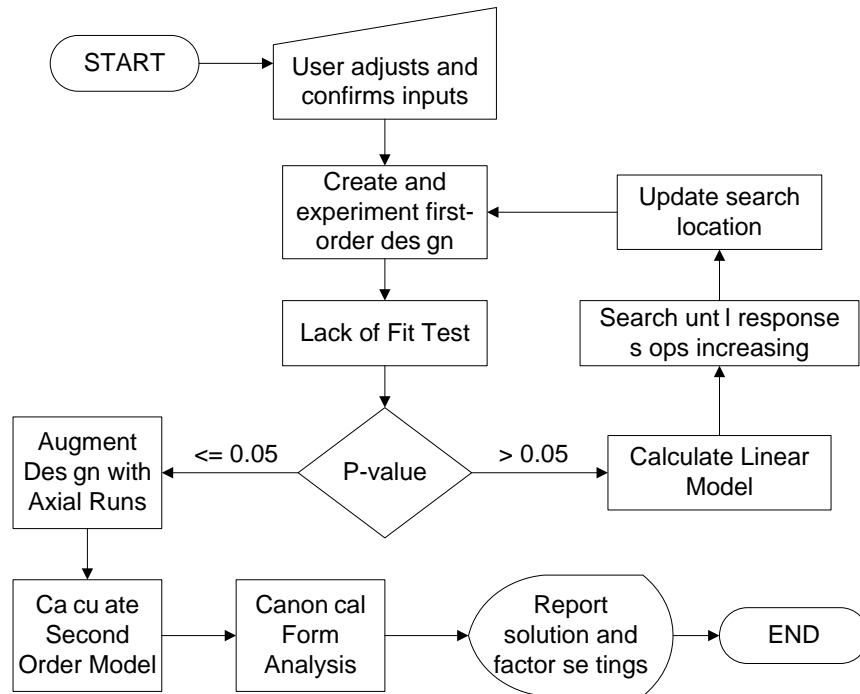


Figure 3.1. RSM Overview Flowchart

The planner updates a status indicator to advance to subsequent stages of the RSM process after experiments are planned for ARES. ARES does not interact with the RSM planner during the experiment process. Every time the user accesses the planner from ARES, the status indicator is retrieved. The status dictates what actions the planner should execute to successfully advance to the next stage or event. These actions typically involve gathering response data, performing necessary calculations, and

displaying the appropriate Graphical User Interface (GUI). Whether the user decides to perform experiments or cancel the planner, the status updates to the appropriate status before the planner exits. The Sections 3.2 through 3.5 explain each possible status indicator and the actions of the program based on each status. Appendix A includes a list of all possible status indicators. Appendix B includes a list of all available data files used in the input/output system.

### **3.2 Initial Start and First Order Design Flow**

The RSM initialization occurs when the status equals “Start”. The flowchart in Figure 3.2 displays the actions of the planner when this status is obtained. The “Start” status can originate from three different possibilities: no previous experimentation, completion of a previous RSM process, or from a manual decision to restart the process. In two of these possibilities, some of the stored data files contain superseded information. Therefore, the first step is to clear all data files except for the file that stores previous RSM results.



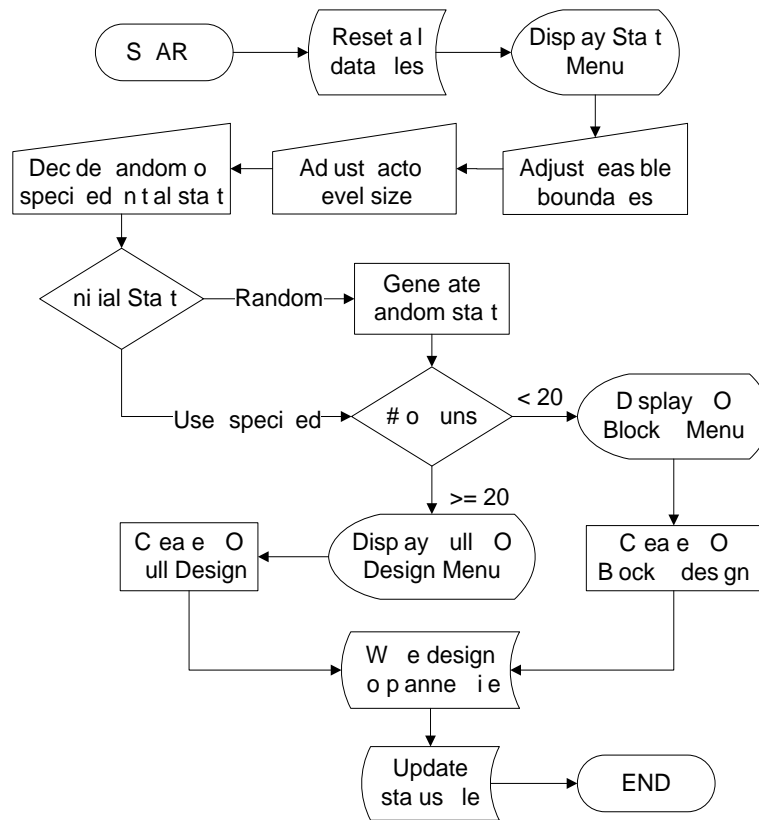


Figure 3.2. Initial Start and First-Order Design Flowchart

The start menu GUI, shown in Figure 3.3, opens immediately after the data files are cleared. The first button opens a spreadsheet that displays the results from previous RSM processes. Analysis of previous results can assist in determining future input settings. The lower section of the start menu contains the buttons that allow the user to alter the input settings. The red notice informs the user that at least ten experiments must be available to advance to the first-order design phase. If less than ten experiments are available, a warning message appears after the user confirms to experiment the first-order design. In that situation, the program will not plan any experiments and there is no change to the status.

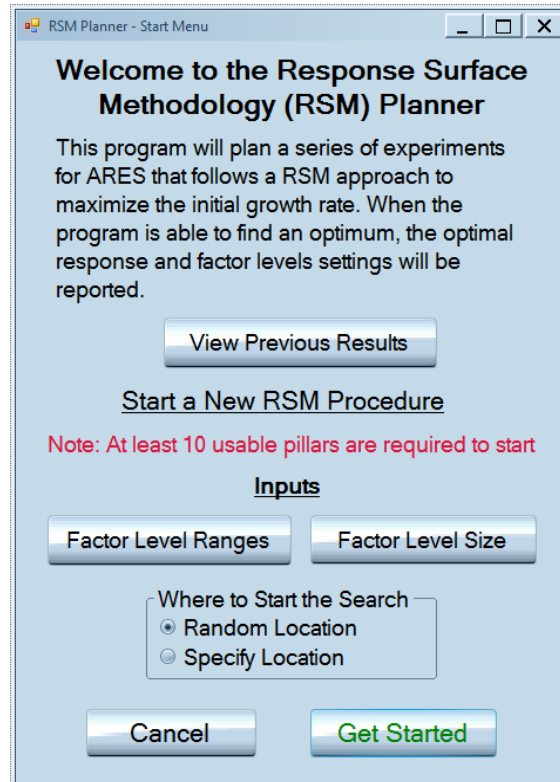


Figure 3.3. Initial Start Menu GUI

The first input button opens another menu to adjust the factor level ranges. The range adjustment menu is shown in Figure 3.4. This menu loads default values for the minimum and maximum ranges provided by the researchers prior to coding the program. There are two common reasons to adjust the factor level ranges. First, the experimental region may expand if the capabilities of the ARES system increase in the future. Second, the user may become disinterested in experimenting in certain areas of design space. The input boxes of the ranges allow the user to type in any text value. These values must be feasible settings that ARES can execute. The program will return an error message if a maximum range is less than a minimum range.

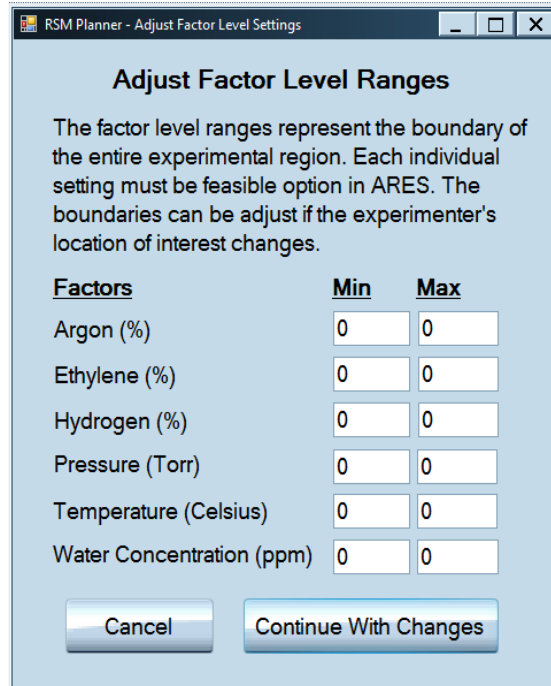


Figure 3.4. Factor Level Range Adjustment Menu GUI

The next input option, shown in Figure 3.5, is the factor level size adjustment menu. This menu also loads default values mostly based on the suspected noise of each factor provided by the researchers. Unlike the factor level range menu, the size adjustment menu displays ratio variables instead of mixture percentages since the mixture three levels cannot change independently. This menu contains numeric textboxes that allow the user to incrementally change the level size values by clicking on the corresponding arrow. The benefit of numeric textboxes is that only numeric values within a predetermined minimum and maximum range can be entered. After several iterations of the RSM process, the user should consider rescaling the factor level sizes. Level sizes should be large enough to overcome noise, but not so large that the effect of a single factor unintentionally dominates the main effects regression model (Montgomery, 2009:256).

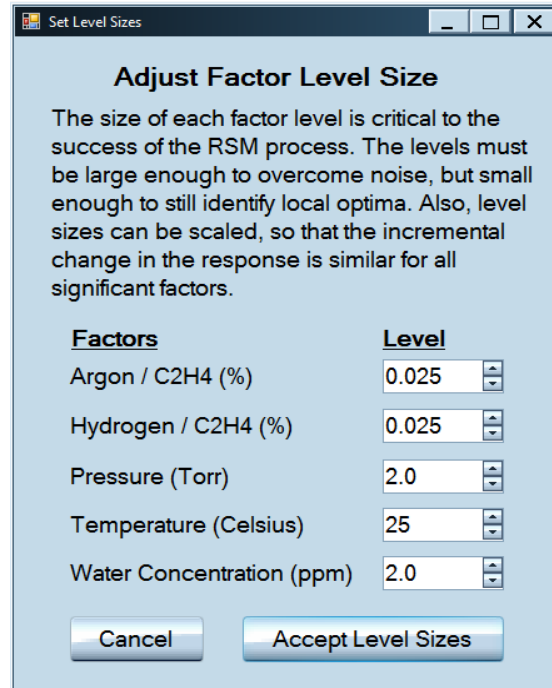


Figure 3.5. Factor Level Size Adjustment Menu GUI

The last user input is the initial search location of the RSM model. The two options available are a random or user-specified location. The random location is generated within the inner sixty percent of the design region to avoid immediately searching near a boundary. The start location menu, shown in Figure 3.6, uses numeric textboxes to input the desired start location. The range of the numeric textboxes adjusts based on the information from the factor boundaries and level size. This adjustment ensures that the initial first-order design is within the region of operability. The selection of the initial location is solely a user preference, but previous research knowledge and RSM results should factor into the decision.

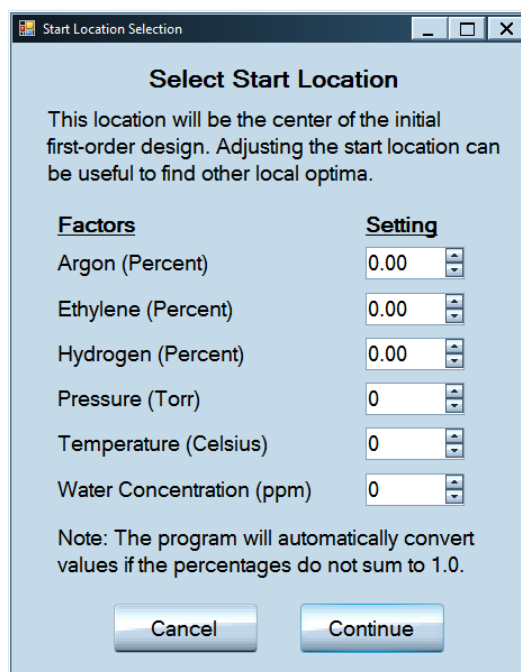
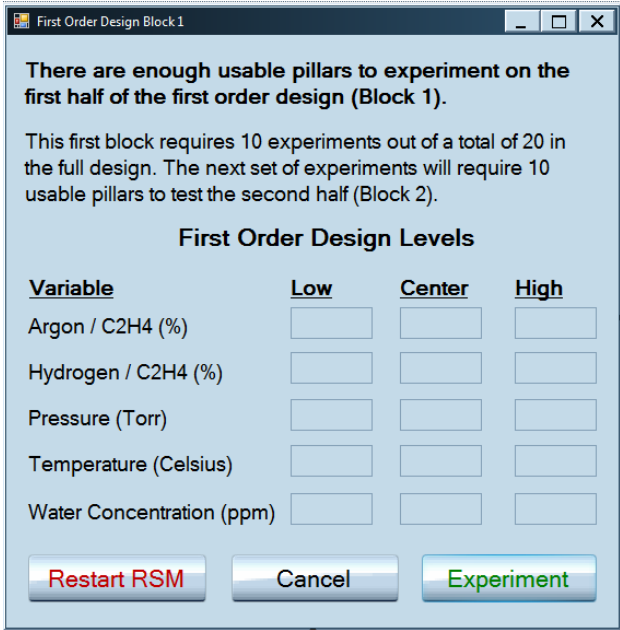


Figure 3.6. User-Specified Start Location Menu GUI

The “Get Started” button is pressed once the user is ready to advance from the start menu. This button has green text to signify that this action will continue the RSM process as recommended by the programmer. Buttons with black text are optional actions that may alter the original model plan. Buttons with red text are inadvisable actions or invoke restarting the entire process. This coloring scheme is intended to help novice users navigate quickly through the GUI of each process.

After the start menu, the number of available experiments determines the next course of action. If the number of available runs is less than 20, the first-order design is executed in two separate orthogonal blocks. Orthogonal blocking limits the nuisance effects created by performing sets of experiments on different patches or at a much different time. When blocking, the first-order block 1 menu appears and informs the user

that a block requires ten runs, as shown in Figure 3.7. This menu displays the three possible factor levels, so the user is aware of the settings tested in this design. If the user selects to continue, the coded first block design is saved to a data file and is also written to the planner file in engineering units. The status is updated to “FO Block 1” to represent that only the first block is complete. The full first-order design menu is displayed when 20 or more runs available. This menu is similar to the first block menu, but reflects the full design. The same actions described in the first block are performed on the full design, but the status is changed to “FO Full” to represent that all first-order runs are complete.



Variable	Low	Center	High
Argon / C2H4 (%)	<input type="text"/>	<input type="text"/>	<input type="text"/>
Hydrogen / C2H4 (%)	<input type="text"/>	<input type="text"/>	<input type="text"/>
Pressure (Torr)	<input type="text"/>	<input type="text"/>	<input type="text"/>
Temperature (Celsius)	<input type="text"/>	<input type="text"/>	<input type="text"/>
Water Concentration (ppm)	<input type="text"/>	<input type="text"/>	<input type="text"/>

Figure 3.7. First-order Block 1 Design Menu GUI

After completing the first block of the first-order design, the “FO Block 1” status is captured upon the next planner access. The planner obtains the response values from the first block and saves these results to the first-order response data file. The second

block menu displays to show the same information as the other two first-order menus. If tens runs are available, the coded design of the second block is appended to the first block design in the data file. The second block is written to the planner file in engineering units. The status updates to “FO Block 2” to represent that the second block of the first-order design is complete. The flowchart that depicts the planner’s actions for a “FO Block 2” status is shown in Figure 3.8.

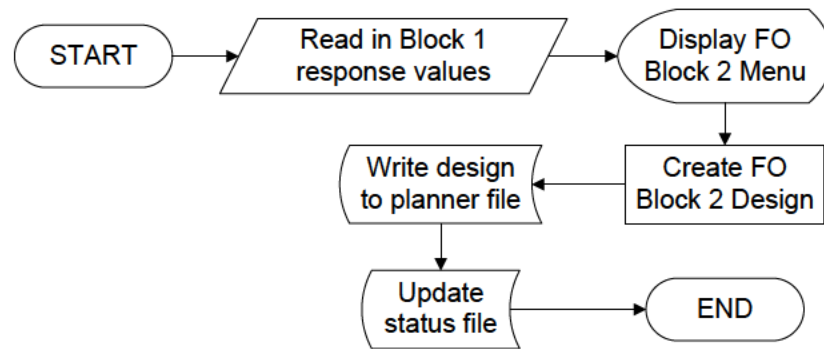


Figure 3.8. First-order Design Block 2 Flowchart

### 3.3 Lack of Fit Test and Post-Results Flow

The lack of fit test and post-results flowchart is shown in Figure 3.9. When status is “FO Full” or “FO Block 2”, first-order design experimentation is finished. If the status is “FO Block 2”, the second block response data is appended to first block results. If the status is “FO Full”, all of the response data is obtained and saved. The lack of fit test is performed using the coded first-order design and the response data. This test returns a p-value which is the deciding factor for the next course of action.

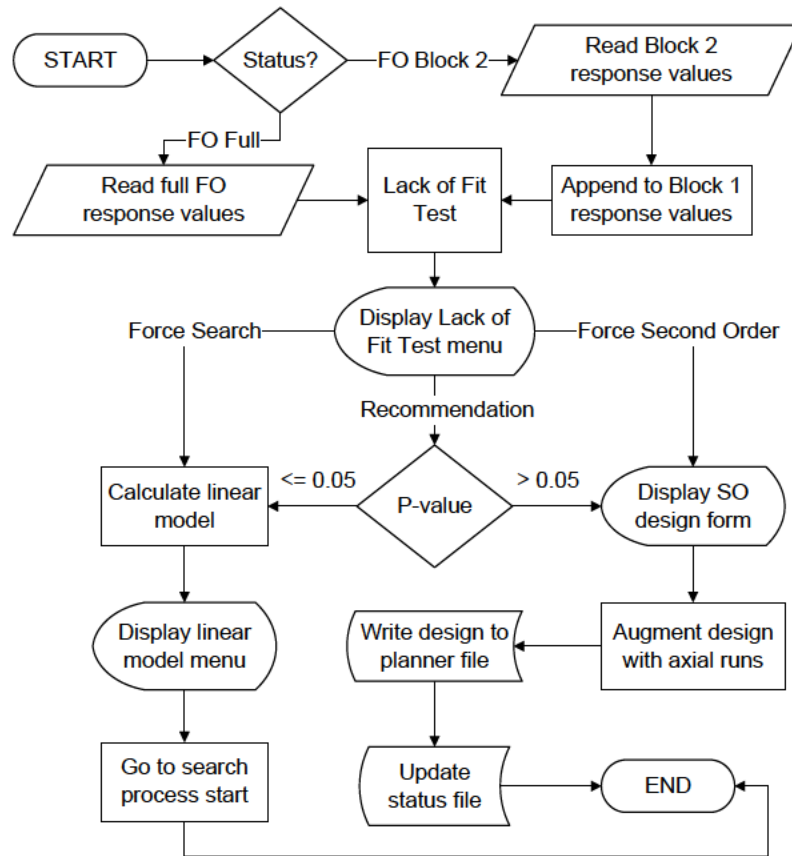


Figure 3.9. Lack of Fit Test and Post-Results Flowchart

The lack of fit test results menu displays the p-value result and several selectable actions, as shown in Figure 3.10. If the p-value is less than or equal to the threshold of 0.05, augmentation to a second-order design is recommended. If the p-value is greater than this threshold, the search process is recommended. To proceed with the recommendation, the user should select the “Experiment with Result” button. The user also has the option to not proceed with the recommendation and force a second-order design or search process. The RSM process can benefit from forcing second-order design augmentation if two search iterations have executed and the maximum response is minimally improving. Forcing the search process requires additional experiments, but



can help to shift the experimentation region closer to the optimal solution. The decision to force either option primarily involves the tradeoff between the accuracy of the final solution estimate and the amount of additional experiments the user is willing to perform.

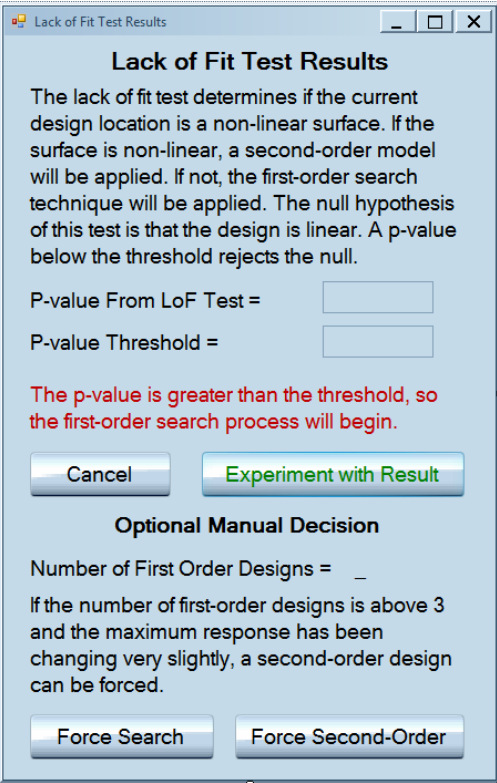


Figure 3.10. Lack of Fit Test Results Menu GUI

To begin the search process, a first-order regression model is required to compute the path of steepest ascent. The model coefficients are calculated by matrix multiplication involving the coded first-order design and the response values. The coefficients and intercept of the first-order model are displayed to the user in the linear regression model menu. The regression menu GUI is shown in Figure 3.11. Due to the log transformation, the results are difficult to interpret. However, the sign and magnitude

of each coefficient still provide great insight into the direction of the path of ascent. Following the regression model menu, the model coefficients are the main input of the search process. Section 3.4 discusses the search process flow.

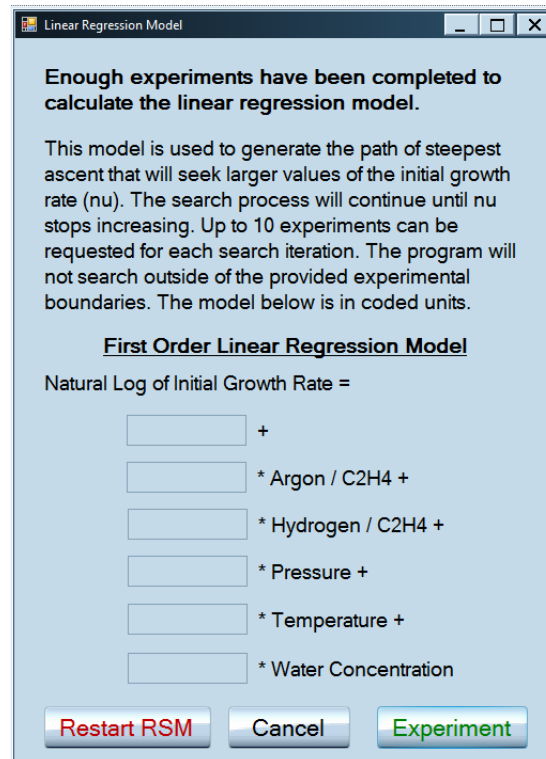
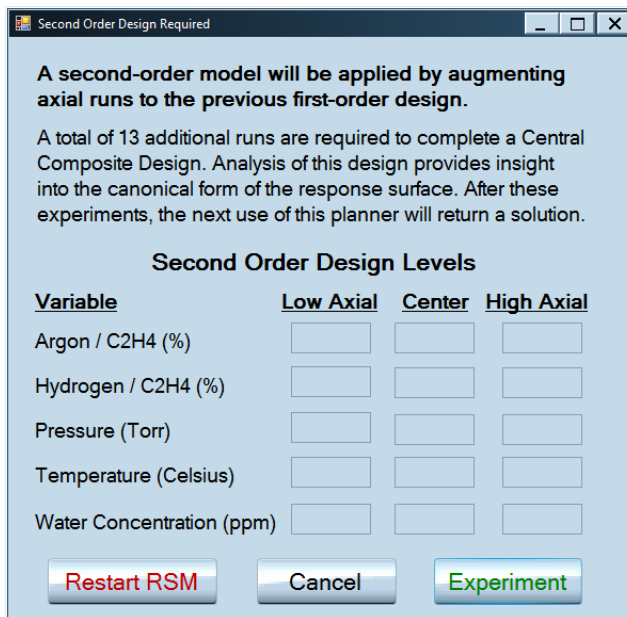


Figure 3.11. Linear Regression Model GUI

The second-order design augmentation process begins with displaying the second-order design menu. This menu is similar to the first-order design menus, but adjusts the low and high levels to reflect the axial distance, as shown in Figure 3.12. The second-order design augmentation involves axial runs and additional center point runs, if applicable. These augmented experiments are first generated in the coded form, randomized, and then saved to a data file. The runs are converted to engineering units and then written to the planner file. The status is updated to “Second Order” to represent

that the second-order design is complete. Section 3.5 discusses the analysis of the second-order design results.



**Second Order Design Required**

A second-order model will be applied by augmenting axial runs to the previous first-order design.

A total of 13 additional runs are required to complete a Central Composite Design. Analysis of this design provides insight into the canonical form of the response surface. After these experiments, the next use of this planner will return a solution.

**Second Order Design Levels**

Variable	Low Axial	Center	High Axial
Argon / C2H4 (%)	<input type="text"/>	<input type="text"/>	<input type="text"/>
Hydrogen / C2H4 (%)	<input type="text"/>	<input type="text"/>	<input type="text"/>
Pressure (Torr)	<input type="text"/>	<input type="text"/>	<input type="text"/>
Temperature (Celsius)	<input type="text"/>	<input type="text"/>	<input type="text"/>
Water Concentration (ppm)	<input type="text"/>	<input type="text"/>	<input type="text"/>

Figure 3.12. Second-order Design Menu GUI

### 3.4 Search Process Flow

The search process consists of three main phases: initialization, analysis, and continuation. Initialization of the search process involves establishing the path of steepest ascent and saving the important search information to data files for later use. The analysis of the search process determines if a maximum value is obtainable from the search results. If no maximum value is found, then the search process continues. When a maximum value is found, a new first-order design is centered at this location and advances the RSM process. The search process initialization flowchart is shown in Figure 3.13.

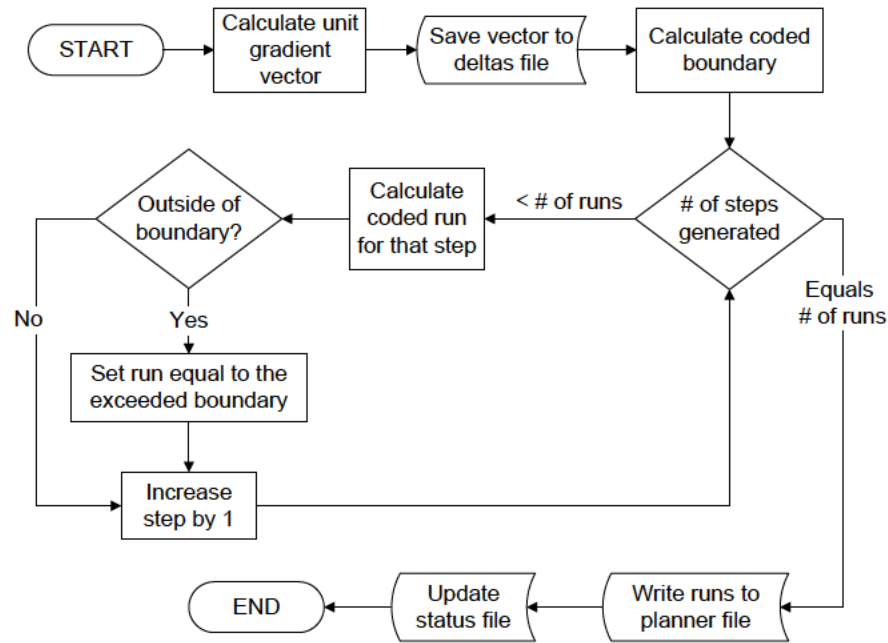


Figure 3.13. Search Process Initialization Menu GUI

### 3.4.1 Search Process Initialization

The search process initialization begins with the calculation of the path of steepest ascent using the unit gradient approach. This path is then stored in a data file, so the same path can be reused if the maximum value is not yet obtainable. The factor level boundaries are calculated in coded form using the current search location and the level sizes. This coded boundary range prevents the search from planning experiments outside of the region of operability. The planner will generate no more than ten experiments during the search phase to limit the amount of unnecessary experiments. After an experiment is generated in coded units, it is compared to the coded boundary range. If any factor level exists outside of this range, that level is set equal to the coded boundary. Experimentation continues on the boundary for the remainder of planned experiments. Section 3.6.3 discusses this boundary technique in greater detail. The coded search

experiments are saved to a data file and then converted to engineering units for the planner file. The status is updated to “Search” to represent that the RSM model is in the search process phase.

### ***3.4.2 Search Process Analysis Phase***

This subsection discusses the search analysis phase. Traditionally, each search process run is analyzed individually against a stopping criterion. Due to the lack of communication between ARES and the planner, streams of experiments are analyzed until a stopping point is established. The flowchart in Figure 3.14 displays the main algorithm for the analysis phase. The first step is to obtain the search response data and then append the data to the previous results from that search, if applicable. It is important to analyze all of the search results together, because data essential to the stopping condition can exist on separate streams of experiments. A loop is applied to analyze each experiment result. The counter for this loop is a step variable which increases by one after each experiment is analyzed. The maximum response value and the step at which it occurs are saved in case the stopping condition is achieved. The stopping condition is achieved when the response value has decreased in two consecutive steps (Myers et al., 2009:182). This stopping criterion is a robust enough to not trigger for extreme outliers in the positive or negative direction.

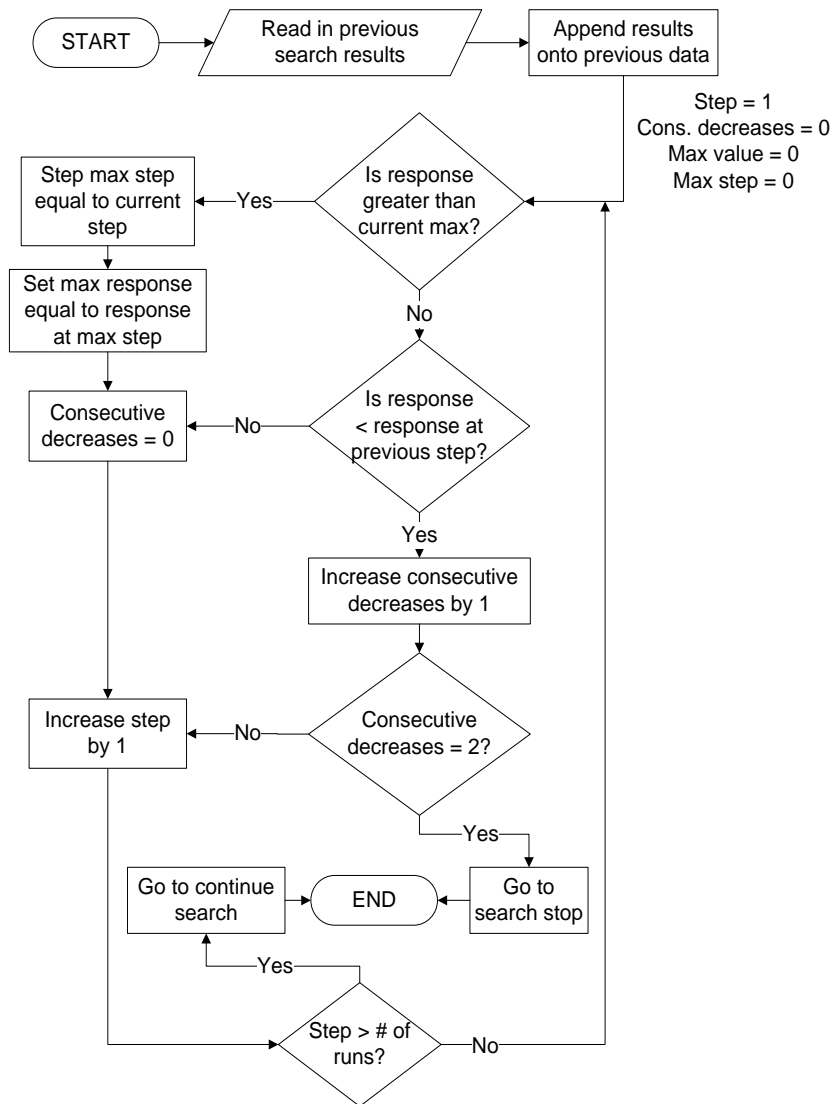


Figure 3.14. Search Process Analysis Phase Flowchart

The analysis loop ends if there are no more experiments to assess or the stopping condition is achieved. If the stopping condition is achieved, the search location with the maximum response becomes the center of a new first-order design. It is possible that the maximum response is located many experiments before the stopping condition. These maximum responses appear as outliers in the positive direction, but should not be overlooked. Narrow peaks in the response surface are hard to identify with large factor

level sizes. The location of the maximum response is updated in data file as the current search location. A menu displays next and informs the user of the current maximum response and location, as shown in Figure 3.15. The new first-order design is generated around this location using the same factor level sizes from the initial start menu. The first-order design procedure is identical to the description from Section 3.2. The status indicator updates to the appropriate first-order status depending on the amount of available experiments.

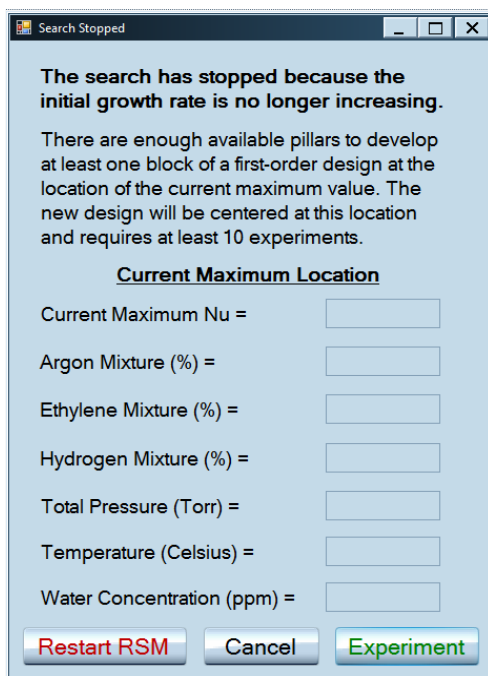


Figure 3.15. Search Process Stopped Menu GUI

### ***3.4.3 Search Process Continuation Phase***

The search process continues if two consecutive decreasing values are not found in the search response results. The flowchart for the continuation phase is shown in Figure 3.16. The first step is to display a menu to inform the user of the continuation of the search process, as shown in Figure 3.17. This menu displays the current maximum

response and the factor level increments of the search. The experiments in this phase are generated in the same manner as the initialization phase. The status indicator remains at “Search” to represent that the search process is still active.

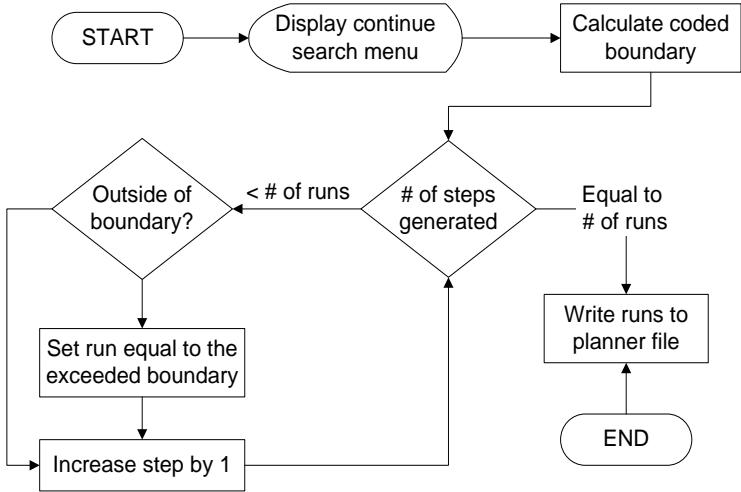


Figure 3.16. Search Process Continuation Phase Flowchart

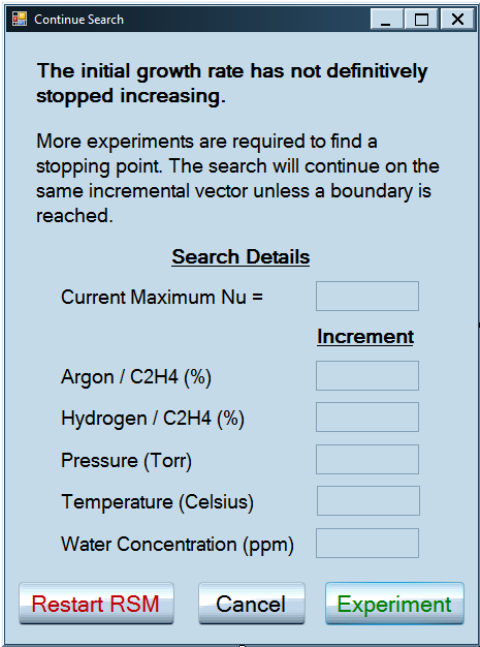


Figure 3.17. Search Continuation Menu GUI



### **3.5 Solution Determination and User Report**

After the axial block is experimented, the remaining steps of the RSM process focus on obtaining an optimal solution. The flowchart for second-order model generation, canonical analysis, and the solution report is displayed in Figure 3.18. The first step is to obtain the augmentation response results from the data file. These results and the augmentation coded design are appended to the previous first-order response results and coded design, respectively. The combination of these two design portions completes the augmentation of the Central Composite Design (CCD). To generate a second-order model, the independent variable matrix must also include interaction and quadratic terms. These additional terms are calculated by multiplication of the proper two main effect columns in the matrix. After this calculation, the second-order model coefficients are generated and then assigned to the appropriate canonical analysis matrix or vector.

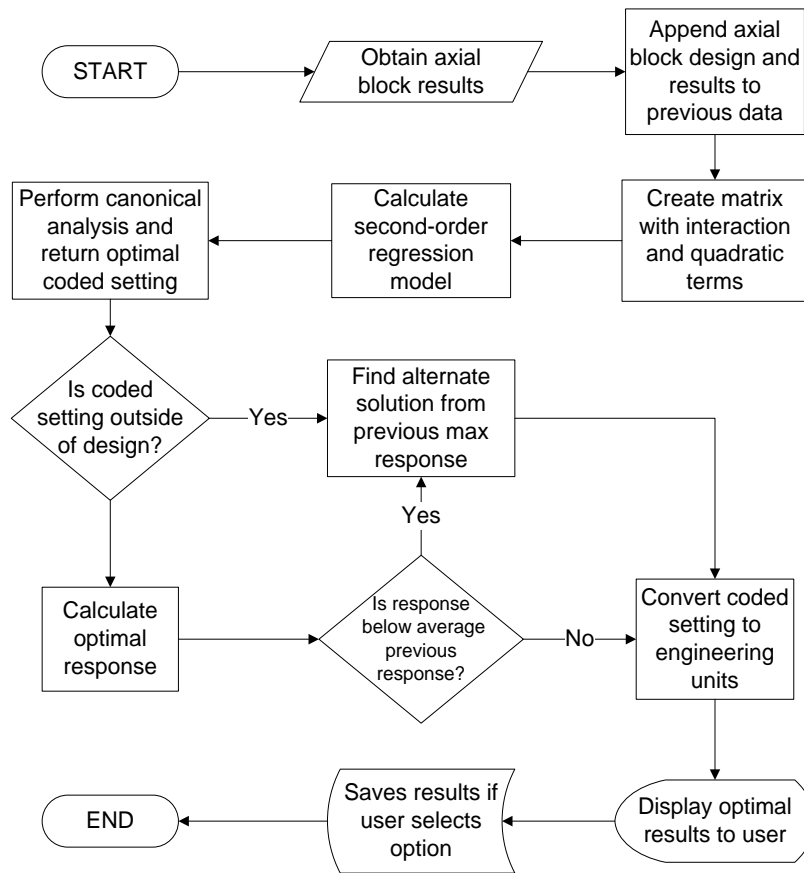


Figure 3.18. Canonical Analysis and Solution Flowchart

The coded stationary point  $x_s$  is obtained through canonical analysis of the second-order model. For this point to be considered the final solution, it must fall within the second-order experimentation region and appear to represent a local maximum. It is possible that the estimated stationary point is located inside the design region, but is still in the canonical form of a minimum or saddle point. A minimum or saddle point response value is likely of no use to the user. Classic analysis uses eigenvalue analysis to classify the response surface. For this tool, the value of the predicted response is compared to the second-order design response data. If the predicted response is less than

the average of the second-order design response data, the canonical form is likely not a maximum. If the canonical analysis appears to not provide a maximum solution, the experiment from the CCD with the largest response value is considered the alternative optimal solution.

A menu displays to report the appropriate solution to the user, as shown in Figure 3.19. The user is informed whether the result is obtained through canonical analysis or from the CCD results. The predicted optimal response and the corresponding factor level settings are displayed. If the user is satisfied with the results, there is an option to save the results to a data file.

Potential Solution for Maximum Initial Growth Rate

**A potential solution has been found for the maximum initial growth rate.**

The goal is to find a canonical form of a local maximum and an optimal solution that is within the bounds of the second-order design. If these goals are met, a true optimal value and location will be listed. If not, an alternative solution from the second-order design is listed.

**Potential Solution:**

Optimal Maximum Nu =

Argon Mixture (%) =

Ethylene Mixture (%) =

Hydrogen Mixture (%) =

Total Pressure (Torr) =

Temperature (Celsius) =

Water Concentration (ppm) =

Figure 3.19. Predicted Solution Report GUI

### **3.6 Additional Challenges of Autonomy Incorporation**

#### ***3.6.1 Experiment Success and Data Capture Rate***

Carbon nanotube experimentation is certainly an arduous process. Numerous nuisances can influence the success of each experiment. These nuisances can hinder the success of an experiment with complete independence from the actual factor level settings of that run. On a regular basis, a set of experiments contains at least one run that did not have successful growth due to extraneous influences on ARES. These unsuccessful runs are usually unrelated to planned factor settings. All stages of the RSM process depend on reliable response data, so it critical to obtain as many successful runs as possible. Eventually, it is more beneficial to advance through the RSM process with some unsuccessful results than continually retest the same design until perfect results are obtained.

The first and last run of each experiment set can produce unreliable or missing results. The researchers do not currently have the ability to perform trial experiments on ARES. Trial experiments can help a system “warm-up” and reach a steady-state performance before the designed experiments begin. The lack of any trial runs or previous experimentation on ARES leads to a high rate of unsuccessful growth on the first designed experiment run. Also, ARES is currently unable to capture growth data on the last run of each designed experiment set, although the researchers can occasionally approximate an initial growth rate of the last experiment. Overall, the issues with the first and last experiment can affect up to 20 percent of the first-order design runs. Yet due to the randomization and the design resolution, the main effect estimates should not alter significantly.

It is also possible that most experiments in a set are unsuccessful. This can occur from a number of nuisances including faulty temperature calibrations or a program memory leak. When a large percentage is unsuccessful, an entire retest is expected. Experimenting in partial sets is not recommended due to the importance of blocking. It is highly preferred that each block is tested on the same patch of silicon pillars. When retesting is required, adjusting the status indicator and the appropriate data files is a difficult for new system user. A methodology must exist to virtually recreate the RSM process to its previous state before the set of unsuccessful experiments. It is critical that the planner does not delete and can recover all of the necessary information to move a step backwards in the process.

### ***3.6.2 Model Adequacy and Outlier Analysis***

In traditional RSM practice, the analyst can validate the assumptions of each linear regression model during the creation. The most critical adequacy checks involve visually assessing the model's residuals. These visual checks are not plausible in an autonomous RSM system. Historical data, if it is available, can be analyzed to foresee if model adequacy is an issue. Data transformations on the response and regressor variables can ensure normality and constant variance of the model's residuals. In this study, a log transformation is applied to the response variable to correct a funnel-shaped trend identified in a constant variance plot. The log transformation was verified on the prior data and can also be further verified using experiments designed from the RSM planner. If residual analysis continually demonstrates that a log transformation is necessary, then regression model assumptions are likely satisfied in future RSM processes.

The planner does not perform any internal outlier analysis. The carbon researchers perform their own analysis on outliers. The analysis primarily involves the determination of whether the extreme value was caused by an error in the ARES system. If response data is deemed invalid by the researcher, it should be adjusted before the planner obtains the value. Statistical outliers may still exist in each linear model, but should not significantly affect coefficient estimates due to the robustness of factorial experimental designs to outliers (Montgomery, 2009:268). Moreover, an outlier in the extreme positive direction could represent a small region where a local maximum exists. If outliers or other nuisance factors are continually problematic, experiment replication in any stage of the RSM process is recommended.

### ***3.6.3 Mathematical and Functional Techniques in C#***

The C# language is limited its mathematical functions and capabilities. Several open-source software packages exist that provide some advanced mathematical techniques, but none of these packages are included in the planner for several reasons. The packages lack a great amount of documentation and instructions. Second, the packages use different object classes. These object classes are not compatible with the mathematical functions and techniques already developed in the planner code. Lastly, it is dangerous to incorporate open-source software into computers on government networks or even on stand-alone units. Many technical functions were developed for C# during the research time period, but there are several techniques that required workarounds due to the lack of capability.

### ***Simplified Boundary Technique.***

During the path of steepest ascent, the search continues along the determined path until it reaches a contact point on a factor level boundary. The contact point typically occurs in between full runs in the search process. For example, the contact point could occur at 5.67 coded steps from the design center which is in between planned runs five and six. The planner increases the integer step counter by one for each experiment. If the contact point experiment is tested, the levels of the unconstrained factors need to be adjusted to reflect a fractional run and the step counter is offset by one. Rather than add this increased complexity, the contact point experiment is skipped and the search resumes at the next full run. The additional effort required to code the contact point experiment outweighs the benefit of including this experiment in the search process. The appropriate constrained path is still followed along the boundary.

The search continues on the boundary until the response stops increasing. When the planner assesses that the boundary is reached and a maximum response is found, the RSM process is considered complete. Normally, a first-order design is centered at the stopping point, but this is not possible on the boundary. Due to the unlikelihood that a new design searches away from the boundary, the maximum search location is considered the final solution. The search boundary location menu displays this final solution to the user, as shown in Figure 3.20. The menu provides a recommendation to restart the process at a different initial start to hopefully find a true optimal solution within the region of operability.

**Search Boundary Reached**

During the search process, at least one of the variables reached the feasible boundary.

Use a different start location to possibly find a true optimal solution within the boundary. If changing the initial settings does not work, the factors on the boundary should be set to a stationary point somewhere inside the boundary.

**Best Result Found on the Boundary**

Maximum Nu =

Argon Mixture (%) =

Ethylene Mixture (%) =

Hydrogen Mixture (%) =

Total Pressure (Torr) =

Temperature (Celsius) =

Water Concentration (ppm) =

Figure 3.20. Search Boundary Solution Menu GUI

### ***Canonical Analysis Without Eigenvalue Capability***

To determine the true nature of the response surface, one could analyze the eigenvalues of the  $\hat{B}$  matrix. With these eigenvalues, there is a greater possibility to correctly label the response surface as a minimum, maximum, saddle point, or a ridge system. However, algorithms for calculating all five eigenvalues of the  $\hat{B}$  matrix are quite difficult in the C# environment. It is still possible to gain insight into the canonical form even without the eigenvalue analysis. The canonical form is likely a minimum or a saddle point if the optimal response value is lower than the average responses from the CCD. A ridge system is likely if the optimal setting is well outside of the CCD region of experimentation. Through a process of elimination, the canonical form is predicted as a



maximum. This alternate procedure is followed after the optimal coded settings are determined. The sign and magnitude of the second-order coefficients can occasionally provide insight into the canonical form, but this is an unreliable technique when interaction terms are significant.

### ***Verification of Planner with Test Distribution***

During the design phase, the planner was coded on a personal computer separate from the ARES system. The RSM requires response data to advance through the process, but true experimentation can only occur after implementation on ARES. To provide simulated results for the planner, a multivariate normal distribution was applied to represent ARES experimentation. Simulated results are crucial for the verification of the planner's algorithms and analytical techniques. The multivariate normal distribution contains only one peak, so the results are fairly easy to interpret. The standard deviation of each variable was large enough to ensure the planner never starts in an area with an extremely flat surface. A normally distributed random error is applied to each response result. It is helpful to start with a low degree of random error and then gradually increase the error after further verification. With a large number of variables, the multivariate normal returns very small probabilities. The probabilities were scaled to larger values to improve recognition of the results and to identify an appropriate random error scale.

## **IV. Results and Analysis**

This chapter presents the results from executing the Response Surface Methodology (RSM) experiment planner on the Adaptive Rapid Experimentation and Spectroscopy (ARES) system. These results are collected to validate the RSM techniques and verify the planner's algorithms on the true system. The operation of the planner was performed under supervision, so full autonomy was not applied for the collection of this data. The operation was supervised, because the planner was still in early stages of development on the ARES system. The supervision did lead to some significant insights regarding the performance of autonomy. These insights are discussed in Chapter 5. Not enough time was available to complete the full RSM process, but significant findings are identified with the available data. This chapter is divided into three sections based on the stages of the RSM process. The first section discusses the initialization and first-order design. The second section discusses the first-order model analysis and the search process. The third section discusses the second first-order design and the proposed search process. The fourth section discusses concerns with laser temperature calibration.

### **4.1 Initialization and First-Order Design**

The first inputs into the planner are the number of available experiments and the type of catalyst. For ease of implementation, the number of runs was hard-coded at ten for each access of the planner. Ten runs were selected as the hard-coded value, because each set of experiments throughout the entire RSM process can be planned at ten runs. For this RSM process iteration, the researchers selected an iron-based catalyst. This catalyst differs from other catalysts because it does not require a cooling agent. The

water concentration variable is not of interest for this RSM process iteration. The software in the planner and ARES is designed to experiment with six total factors, so a planned setting for water concentration is required in the planner file. The level size is set to zero, so the actual water concentration is planned at the initial location value of 3 parts per million (ppm) and never changes for each experiment. Actually, no water is applied to the catalyst and the 3 ppm merely satisfies the software. Any effect attributed to water in the first-order model is just due to noise. Table 4.1 displays the initialization settings used. A user-specified initial location was selected with the mixture gases initialized at an almost equal blend.

Table 4.1. RSM Process Initialization Settings

	<b>Ratio 1 (Ar / C<sub>2</sub>H<sub>4</sub>)</b>	<b>Ratio 2 (H<sub>2</sub> / C<sub>2</sub>H<sub>4</sub>)</b>	<b>Pressure (Torr)</b>	<b>Temp. (Celsius)</b>	<b>Water (ppm)</b>
<b>Initial Location</b>	0.9706	0.9706	20	725	3
<b>Lower Bound</b>	0.0526	0	1	600	0
<b>Upper Bound</b>	9	8.5	40	1,100	80
<b>Level Size</b>	0.1	0.1	3	40	0

The first-order design was created in two blocks due to the number of available experiments. Each block was executed in a random run order. The coded design settings and the response results for the appended first-order design are displayed in Table 4.2. This table also includes a column for notes that explains the success of each experiment. The first experiment of the first block did not show significant growth which is expected when no trial runs are performed. The 17th experiment was the only other experiment to not exhibit growth. Both results are valid according to the research expert, so the low initial growth rate values are maintained. The last experiment likely had successful

growth, but the result data was not saved due to a malfunction within ARES. The median response of the other 19 experiments is used as a replacement value for the last experiment. While better techniques exist to replace a missing value in a factorial design, the median was a quick solution used to advance the RSM process. The median was used to not significantly affect the first-order model with another extreme low value, although the design is quite robust to outliers. The quality of fit in the notes of Table 4.2 refers to how well the growth curve fit the G-band data in the opinion of the research expert.

Table 4.2. Coded First-Order Design 1 and Results

Run	Ratio 1	Ratio 2	Press.	Temp.	Water	Block	Response ( $\nu$ )	Notes
1	-1	-1	1	-1	-1	1	4.15	No growth
2	1	1	-1	-1	1	1	136.37	Good fit
3	1	1	1	-1	-1	1	85.97	Good fit
4	0	0	0	0	0	1	84.82	Good fit
5	0	0	0	0	0	1	72.16	Good fit
6	-1	1	-1	1	1	1	114.14	Good fit
7	1	-1	-1	1	1	1	31.81	Good fit
8	-1	1	1	1	-1	1	41.29	Good fit
9	-1	-1	-1	-1	1	1	50.94	Good fit
10	1	-1	1	1	-1	1	13.00	Good fit
11	-1	1	-1	-1	-1	2	654.45	Good fit
12	0	0	0	0	0	2	86.21	Good fit
13	-1	1	1	-1	1	2	68.67	Good fit
14	1	1	-1	1	-1	2	124.97	Good fit
15	-1	-1	-1	1	-1	2	62.21	Good fit
16	0	0	0	0	0	2	28.32	Good fit
17	1	-1	1	-1	1	2	0.11	No growth
18	1	-1	-1	-1	-1	2	38.10	Okay fit
19	-1	-1	1	1	1	2	91.73	Good fit
20	1	1	1	1	1	2	68.67	Median

## 4.2 First Linear Regression Model and Search

The first verification of interest is the log transformation of the response in the first-order model. The main effects model with and without the transformation is generated to show that the transformation effectively stabilized variance. Figure 4.1 displays the untransformed model's residual by predicted response plot. It is obvious in this plot that the variance of the residuals is not constant. Figure 4.2 displays the transformed model's residual by predicted response plot. In this second plot, the variance appears to have stabilized considerably.

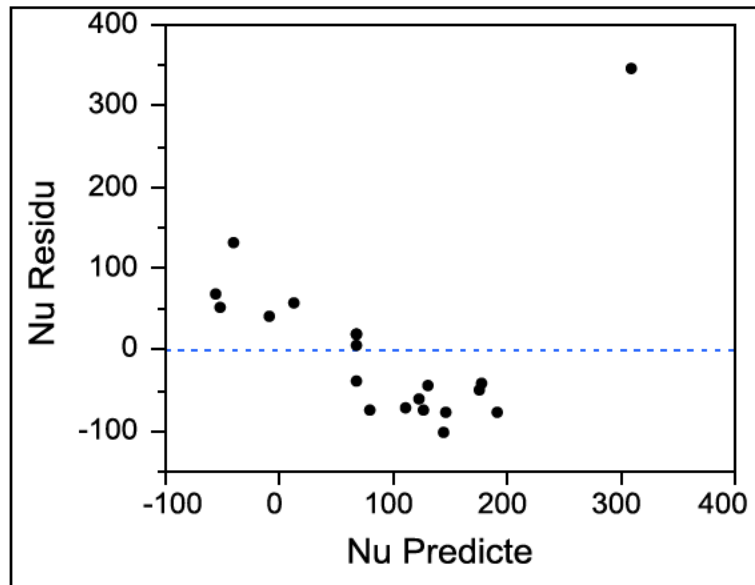


Figure 4.1. Residual by Predicted Response Plot before Transformation

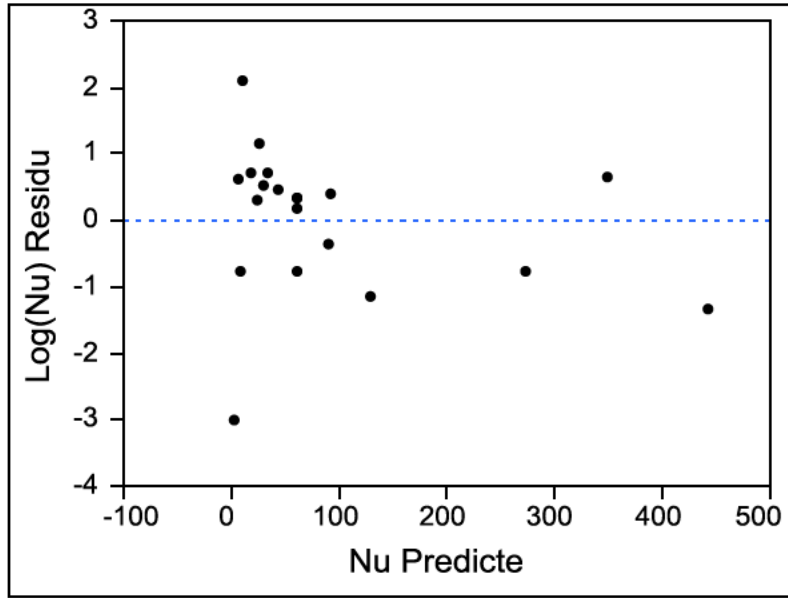


Figure 4.2. Residual by Predicted Response Plot after Transformation

The parameter estimates for the first-order model are generated with the coded design matrix and the log transformed response values. Table 4.3 displays the parameter estimates for the five main effects in the model and the intercept. This table also displays the results of the lack of fit test for pure quadratic error and a significant two-factor interaction for Ratio 2 with temperature. The design is orthogonal, so including these additional estimates does not affect the main effect estimates, but the p-values are slightly different. The t-test ratios and the p-values show which effects are significant in this experimental region.

Table 4.3. Linear Model 1 Analysis and Lack of Fit Test

Parameter	Estimate	t Ratio	Prob >  t
Intercept	3.9119	11.65	<.0001
Ar / C <sub>2</sub> H <sub>4</sub>	-0.4529	-1.51	0.1596
H <sub>2</sub> / C <sub>2</sub> H <sub>4</sub>	1.0060	3.35	0.0065
Pressure	-0.8219	-2.74	0.0193
Temperature	0.3299	1.10	0.2953
Water Concentration	-0.2118	-0.71	0.4953
Lack of Fit Test	-0.2181	-0.65	0.5292
H <sub>2</sub> / C <sub>2</sub> H <sub>4</sub> *Temp.	-0.6508	-2.17	0.0530
Block	0.0114	0.04	0.9669

The results show that Ratio 2 and total pressure are the most significant main effects. Thus, these two effects are the strongest contributors to the main direction of the path of steepest ascent. Ratio 1 and temperature are not significant effects, so the search path will not greatly change for either variable. The lack of fit test returns a negative parameter estimate and a high p-value, so there is virtually no indication of a local maximum in this region. The two-factor interaction is interesting, because it contradicts the direction of the main-effects that comprise it. Due to this twisting of the response surface caused by interactions, it is likely that more than one search iteration is needed to optimize all factors. Although the water concentration effect is only modeling noise, the planner still incorporates this estimate into the path of steepest ascent calculation. The path's direction for the other factors is not altered, but the search increments decrease in size. Also, examination of the blocking factor for this design revealed that it is not a significant effect.

The path of steepest ascent begins at the center of the first-order design which is always the initial search location for the first path. The search increment is calculated

using the main effect estimates and the factor level sizes. Table 4.4 displays the planned experimental design for ten runs of the search path. The response results and notes are displayed on the right side of this table.

Table 4.4. Search Process Design 1 and Results

	<b>Ratio 1</b>	<b>Ratio 2</b>	<b>Press. (Torr)</b>	<b>Temp. (Celsius)</b>	<b>Water (ppm)</b>	<b>Response (<math>\nu</math>)</b>	<b>Notes</b>
<b>Search <math>\Delta</math></b>	-0.032	0.070	-1.72	9.22	0.00		
<b>Base</b>	0.971	0.971	20	725	3		
<b>Run 1</b>	0.939	1.041	18.28	734.22	3.00	3.93	No growth
<b>Run 2</b>	0.907	1.111	16.55	743.45	3.00	8.40	Weak fit
<b>Run 3</b>	0.876	1.182	14.83	752.67	3.00	33.14	Good fit
<b>Run 4</b>	0.844	1.252	13.11	761.90	3.00	25.06	Good fit
<b>Run 5</b>	0.812	1.322	11.38	771.12	3.00	19.02	Good fit
<b>Run 6</b>	0.781	1.393	9.66	780.35	3.00	18.51	Good fit
<b>Run 7</b>	0.749	1.463	7.93	789.57	3.00	10.29	Good fit
<b>Run 8</b>	0.717	1.533	6.21	798.80	3.00	5.29	Good fit
<b>Run 9</b>	0.686	1.603	4.49	808.02	3.00	2.00	No growth
<b>Run 10</b>	0.654	1.674	2.76	817.25	3.00	1.00	No data

The first two runs did not have fully successful growth. The lack of strong growth was attributed to nuisances within the ARES system. The first run is within the original design region and is typically used as a confirmation run, so the lack of true growth data is not much of a concern. The remainder of the results clearly shows that the stopping conditions are achieved and third run contains the maximum response. However, it is possible that the first or second run would have been the actual maximum if reliable growth data was available.

The search experiments were performed on a different patch than the first-order design experiments which could explain why the response values are much lesser in



magnitude than before. The lesser response values could represent that the search path traveled in the wrong direction, but this is unlikely due to the high significance and insensitivity of the linear model. The distance between the second and third runs is very close, so there is not much impact by selecting the third run as the maximum response over the second run.

#### **4.3 Second First-Order Design and Proposed Search**

The next stage of the RSM process is to experiment with another first-order design centered on the location of the third run from the search phase. Due to several issues with the ARES system that caused unsuccessful experiments, the RSM process required a restart to correct the status and data files. The maximum location from the search was inserted as the user-specified initial location, but with some slight rounding corrections. The factor level sizes and boundaries remained the same. Table 4.5 displays the second coded first-order design and the response results. The experimentation of this design also had multiple issues with unsuccessful runs. Due to the limitations in time and experiments, the blocking principle was disregarded to have the ability to obtain four additional data points. If the planned run order is different from the actual run order, it is shown in parentheses in Table 4.5. The planned and actual blocks are displayed in the same format.

Table 4.5. Coded First-Order Design 2 and Results

Run Order	Ratio 1	Ratio 2	Pres.	Temp.	Water Conc.	Resp. (v)	Block	Notes
1	0	0	0	0	0	76.29	1	Good fit
2	1	-1	-1	1	1	47.16	1	Good fit
3	0	0	0	0	0	56.80	1	Good fit
4	1	1	-1	-1	1	57.89	1	Good fit
5	-1	-1	-1	-1	1	47.59	1	Good fit
6	-1	-1	1	-1	-1	39.02	1	Good fit
7	1	-1	1	1	-1	45.35	1	Good fit
8	-1	1	1	1	-1	31.71	1	Good fit
9 (12)	0	0	0	0	0	97.33	2	Weak fit
10 (13)	1	-1	1	-1	1	237.67	2	Good fit
11 (14)	1	1	-1	1	-1	23.35	2	Good fit
12 (15)	-1	1	1	-1	1	45.00	2	Good fit
13 (16)	0	0	0	0	0	34.50	2	Okay fit
14 (17)	-1	-1	-1	1	-1	114.96	2	Good fit
15 (19)	-1	1	-1	-1	-1	16.82	2	Good fit
16 (9)	1	1	1	-1	-1	16.00	3 (1)	Estimation
17 (10)	-1	1	-1	1	1	41.00	3 (1)	Estimation
18 (11)	1	1	1	1	1	42.00	3 (2)	Estimation
19 (18)	-1	-1	1	1	1	38.00	3 (2)	Estimation
20	1	-1	-1	-1	-1	61.65	2	Prediction

The first block included eight out of ten successful experiments and the second block included seven out of ten successful experiments. All five of the unsuccessful experiments are factorial runs. The loss of five factorial runs could significantly impact the linear model estimates, so four of these runs were executed in a separate block. The last run was not obtainable, so a predicted response value is used from a linear model created with the 19 successful runs. Again, better techniques may exist to replace a missing value, but this approach was used as a quick solution on the ARES system. The

additional four runs were executed on the same patch as the second block runs. The researcher manually estimated the initial growth rates for these four runs.

The linear model of the second first-order design is displayed in Table 4.6. Normally, the planner executes the lack of fit test before determining if another linear model is necessary, but it is calculated simultaneously with the linear model for the purpose of this analysis. The lack of fit test effect estimate is negative, so there is no indication that the current experimental region is a local maximum. Only Ratio 2 is a significant effect estimate in this second linear model. The total pressure is no longer a significant variable, so within the current region of experimentation the response is no longer affected by changes to this variable. Pressure may become significant after more searches, but current maximization of this variable demonstrates the effectiveness of the search process. The Ratio 2 coefficient is opposite from the previous direction which is likely due to the significant interaction term in the previous linear model. No interaction terms are significant for this model, so the true path of steepest ascent should now lack curvature.

Table 4.6. Linear Model 2 Analysis and Lack of Fit Test

Parameter	Estimate	t Ratio	Prob. >  t
Intercept	3.9582	25.07	<.0001
Ar / C <sub>2</sub> H <sub>4</sub>	0.0795	0.56	0.5832
H <sub>2</sub> / C <sub>2</sub> H <sub>4</sub>	-0.3531	-2.5	0.0265
Pressure	0.0021	0.01	0.9886
Temperature	-0.0294	-0.21	0.8382
Water Concentration	0.2246	1.59	0.1357
Lack of Fit Test	-0.1651	-1.05	0.3146

There was not enough time to conduct further experimentation and provide results for the second search process in this study. The planned search design for ten runs is displayed in Table 4.7. It is clear from the search design that the primary objective is the optimization of the hydrocarbon gas mixture blend. The pressure barely increases and the temperature slightly decreases. The temperature was originally set at 725 degrees, so it possible that a true optimal exists somewhere in between 725 and 750 degrees.

Table 4.7. Search Process 2 Design

	<b>Ratio 1</b>	<b>Ratio 2</b>	<b>Pressure (Torr)</b>	<b>Temp. (Celsius)</b>	<b>Water (ppm)</b>
<b>Search <math>\Delta</math></b>	0.019	-0.083	0.01	-2.76	0.00
<b>Base</b>	0.879	1.182	15.00	750.00	3.00
<b>Run 1</b>	0.897	1.099	15.01	747.24	3.00
<b>Run 2</b>	0.916	1.016	15.03	744.49	3.00
<b>Run 3</b>	0.935	0.934	15.04	741.73	3.00
<b>Run 4</b>	0.953	0.851	15.06	738.98	3.00
<b>Run 5</b>	0.972	0.768	15.07	736.22	3.00
<b>Run 6</b>	0.990	0.686	15.09	733.47	3.00
<b>Run 7</b>	1.009	0.603	15.10	730.71	3.00
<b>Run 8</b>	1.028	0.520	15.12	727.96	3.00
<b>Run 9</b>	1.046	0.438	15.13	725.20	3.00
<b>Run 10</b>	1.065	0.355	15.14	722.45	3.00

The search design in terms of the actual mixture variables in displayed in Table 4.8. The search increases argon at the expense of hydrogen, while also slowly increasing ethylene. The research expert agreed that lower allocations of hydrogen could improve growth results based on previous experience (Nikolaev et al., 2015).

Table 4.8. Search Process 2 Design for Mixture Variables

	<b>Argon (%)</b>	<b>Ethylene (%)</b>	<b>Hydrogen (%)</b>
<b>Base</b>	0.287	0.327	0.386
<b>Run 1</b>	0.299	0.334	0.367
<b>Run 2</b>	0.312	0.341	0.347
<b>Run 3</b>	0.326	0.349	0.326
<b>Run 4</b>	0.340	0.357	0.303
<b>Run 5</b>	0.355	0.365	0.280
<b>Run 6</b>	0.370	0.374	0.256
<b>Run 7</b>	0.386	0.383	0.231
<b>Run 8</b>	0.403	0.392	0.204
<b>Run 9</b>	0.421	0.403	0.176
<b>Run 10</b>	0.440	0.413	0.147

#### 4.4 Laser Temperature Calibration Concerns

During the experimentation process, concerns arose about the laser temperature calibration. The actual calibrated temperatures are regularly much different from the planned temperatures. The effect estimate for temperature is highly dependent on assumption that the planned and actual temperatures are close to equivalent. However, analysis of the linear models using true calibrated temperatures rather than planned temperatures displayed no significant impact on effect estimates. The calibrated temperatures are usually greater than the planned temperatures, so a discrete offset may exist between planned and true temperature values. The planned and actual temperature settings are displayed in Table 4.9. The average difference between planned and actual temperatures is approximately 41 degrees. The two sets have a correlation of approximately 0.63. The planner could be designed in the future to incorporate the true temperatures, but this compromises the orthogonality of the design.

Table 4.9. Planned and Actual Laser Temperatures

<b>Run Order</b>	<b>Planned Temp. (Celsius)</b>	<b>Actual Temp. (Celsius)</b>	<b>Temp. Difference (Celsius)</b>
<b>1</b>	750	782.92	32.92
<b>2</b>	790	828.37	38.37
<b>3</b>	750	770.78	20.78
<b>4</b>	710	785.53	75.53
<b>5</b>	710	780.19	70.19
<b>6</b>	710	773.89	63.89
<b>7</b>	790	851.45	61.45
<b>8</b>	790	877.80	87.80
<b>9</b>	750	844.01	94.01
<b>10</b>	710	763.71	53.71
<b>11</b>	790	805.09	15.09
<b>12</b>	710	713.31	3.31
<b>13</b>	750	809.33	59.33
<b>14</b>	790	768.11	-21.89
<b>15</b>	710	789.47	79.47
<b>16</b>	710	720.00	10.00
<b>17</b>	790	800.00	10.00
<b>18</b>	790	790.00	0.00
<b>19</b>	790	820.00	30.00

## **V. Conclusion and Future Research**

This chapter discusses the main conclusions from this study. The conclusions are based on the verification of the Response Surface Methodology (RSM) experiment planner, the performance of the autonomy on the Adaptive Rapid Experimentation and Spectroscopy (ARES) system, and the optimization of the carbon nanotube growth response. This chapter includes recommendations on future carbon nanotube experimentation and RSM models. Lastly, ideas for future research on this topic are presented in this chapter.

### **5.1 Summary of Conclusions**

The planner's ability to execute the RSM process was verified through pretesting and with data from the true system. The results of the analytical techniques are verified by matching results from the planner with the data analysis from Chapter 4. The planner's algorithms correctly identified the appropriate status indicators and completed the necessary actions as designed. Input and output data storage operated effectively on the ARES system.

Many difficulties of conducting fully autonomous experimentation were not identified until after the RSM planner was implemented into the ARES system. The planner does not currently have the capability to perform well when the rate of unsuccessful experiments is high. The status indicator technique updates after experiments are planned, but the planner does not have a means of knowing if the experimentation failed due to the one of the many nuisances within ARES. During the

supervised experimentation, the status and data files were manually corrected to resume the RSM process at the appropriate stage. The ARES system does not currently have the capability to retest the experiments in the planner file without accessing the planner. The researchers control what response results are inputted into the planner, so full autonomy is expected as long as the appropriate results are provided. The current performance of autonomy is acceptable, but can greatly improve with the incorporation of the future research ideas presented later in this chapter.

Results from the actual RSM experimentation revealed that the optimization process is operating as expected. The first search process identified multiple significant effects on the initial growth rate. This search appears to have identified a potential optimal setting for total pressure at 15 Torr. Currently, the process is primed for a second search process that aims to find the optimal blend of mixture variables. No interaction effects are significant for the second search, so the path should follow the true response gradient better than the first search process. The only major experimental concern is the temperature setting, because of the inaccuracy of the laser temperature calibration. However, the effect estimates for temperature do not seem largely affected by the inaccuracy. The second search process may also pinpoint the optimal planned temperature setting.

## **5.2 Recommendations**

The first few experiments in a set seem to have a higher rate of unsuccessful growth than the rest of the design. The researchers do not always perform trial or warm-up runs on the ARES system to help ensure that the critical experiments are exhibiting



growth. A simple recommendation is to perform “warm-up” runs before serious experimentation. The system can reach a steady-state performance and hopefully provide a higher rate of successful experiments. The loss of results for several experiments can significantly impact the results of the regression models and the lack of fit test.

The planners installed on ARES are the only methods available to experiment with multiple runs. If several experiments failed in a set, the researchers do not have an ability to immediately retest the unsuccessful runs. Also, if the entire experiment set fails, the experimental design that is already written to the planner file cannot be retested. The first recommendation to solve this issue is to develop an interface where multiple experiments can be entered manually. The warm-up runs can be planned through this interface, as well. The second recommendation is to add the capability to initiate the retesting of the design already in the planner file.

Before implementing the planner on the ARES system, the planner’s algorithms and analytical techniques were tested using a multivariate normal distribution. This distribution is easy to code within any software language. The multivariate normal distribution only has one peak, so it is easy to interpret the results and debug the software. For similar problems that involve creating an RSM computer program, the multivariate normal distribution is an effective way to verify the algorithms and techniques.

### 5.3 Future Research in this Area

#### *Advanced Techniques in C#*

As mentioned in previous chapters, the planner is limited in several areas due to the short amount of time allotted to develop mathematical techniques in C#. A function to find the eigenvalues of a matrix will improve the canonical analysis. Additional coding is required within the search process to add the contact point experiment to the boundary technique algorithm. The assumptions of the regression models are not validated within the planner. It is possible that certain algorithms could analyze the residuals of the model and grade the model's ability to meet assumptions. Lastly, more advanced data storage techniques could assist in saving and applying additional RSM data such as different experimental designs.

#### *Increase Robustness of Status System*

The status indicator technique advances through the RSM process based on the assumption that experiments are successful. The status always advances to the next stage after experiments are planned. This occurs even when the set of experiments is widely unsuccessful. The status system can improve with additional algorithms that analyze response results for unsuccessful experiments. Afterwards, the planner can either create models with only the successful data or decide to retest the unsuccessful experiments. This status system improvement will also require more thought on how response results are provided to the planner. The response results must be listed in the appropriate order, so if an experiment is unsuccessful some sort of placeholder should be used to annotate the problem.

### ***Additional Functionality to Research Different Problems***

The planner is specifically created for the current carbon nanotube growth research problem. The planner can experiment on fewer factors, but not does update the experimental design to the most efficient for that situation. With additional functionality, the user of the planner can select the amount of mixture and process variables to execute RSM on any research problem. Also, researchers have other response variables of interest, so the planner can evolve to a multi-objective response optimization. The planner's software is adaptable for any experimental system that requires response optimization.

### **5.4 Closing Remarks**

The AFRL researchers provided feedback that supported many aspects of the RSM planner. The researchers are pleased with maximization of gas variable flow rates and various user interface menus. The optimization capability is highly desired and appears on track to produce significant findings. There is an interest to incorporate the ARES software into other systems at the Air Force Research Laboratory. The RSM planner software is likely to accompany ARES and be adapted to optimize critical responses of other research problems. Research will continue on the autonomy aspect of the planner. The primary goal is to eliminate the researcher's need to make difficult decisions regarding experiment plans.

## Appendix A

Table A.1. List of Status Indicators and Explanations

Status Indicator	Explanation
Start	New RSM process or after completion
FO Full	Entire first-order design planned
FO Block 1	First-order design Block 1 planned
FO Block 2	First-order design Block 2 planned
Search	Search process runs planned
Continue Search	Resume search process (search menu cancel)
Pre Search	Start search process (lack of fit menu cancel)
Pre Axial	Start second-order design (lack of fit menu cancel)
Second Order	Second-order design augmentation planned

## Appendix B

Table B.1. List of Data Files and Explanations

<b>Data File</b>	<b>Explanation</b>
Catalyst	Name of the catalyst for the current process
Current Location	Current search location or center of first-order design
First Order Coded	Current coded first-order design
First Order Response	Current first-order design response values
Full Levels	Factor level boundaries from the initialization
Initial Start	Initial search location from the initialization
Level Size	Initial factor level sizes from the initialization
Number of Models	Tracks the number of first-order models
Planner	File that experiments are written to - main ARES input
Previous Results	Stores previous RSM process results
Response	File that results are saved to - main planner input
Search Coded	Coded design of search experiments
Search Deltas	Search gradient vector
Search Response	Array of search experiment results
Second Order Coded	Coded design of axial runs
Status	Status indicator files

# Autonomous Experimentation of Carbon Nanotube Growth Using Response Surface Methods

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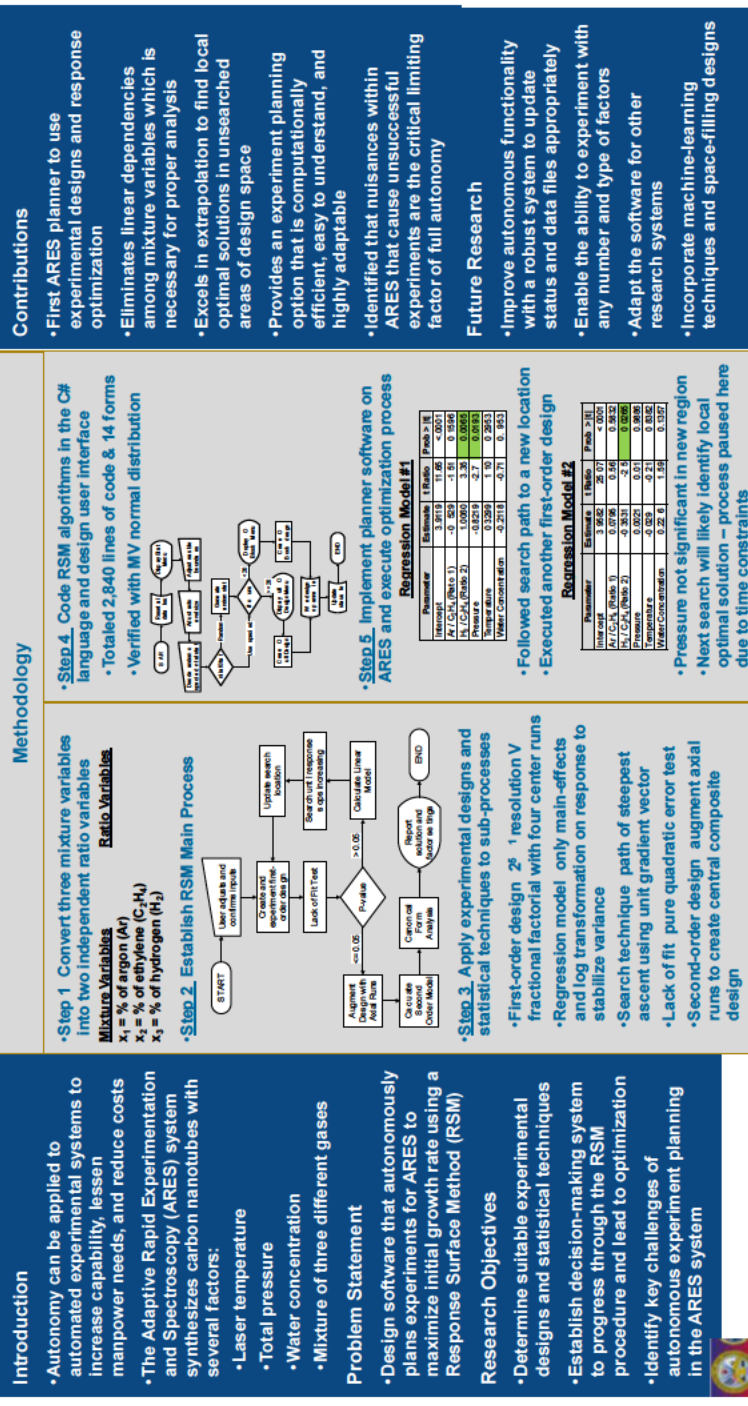


Figure C.1. Storyboard Chart

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14. ABSTRACT Advances in hardware and software technology have led to the development of automated research systems. The Air Force Research Laboratory (AFRL) utilizes the Adaptive Rapid Experimentation and Spectroscopy (ARES) system to synthesize carbon nanotubes. The AFRL researchers are investigating different approaches that can improve the experimental capability of ARES from automation to autonomy. Carbon nanotubes are discussed as an emerging technology for many applications, but AFRL has yet to discover what factors optimize the nanotube initial growth rate. In this study, experimental planning software was written for ARES that autonomously designs and executes experiments based on the Response Surface Methodology (RSM). RSM is a statistically-based method of sequentially planning experiments to find the optimal settings of independent variables that optimize the value of a dependent response variable. This thesis discusses the development and early success of the initial version of the planning software. As this is a relatively new research area spurred by recent advancements in materials research technology, detailed discussion is also provided on the unique challenges of creating autonomous research robots.					
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